

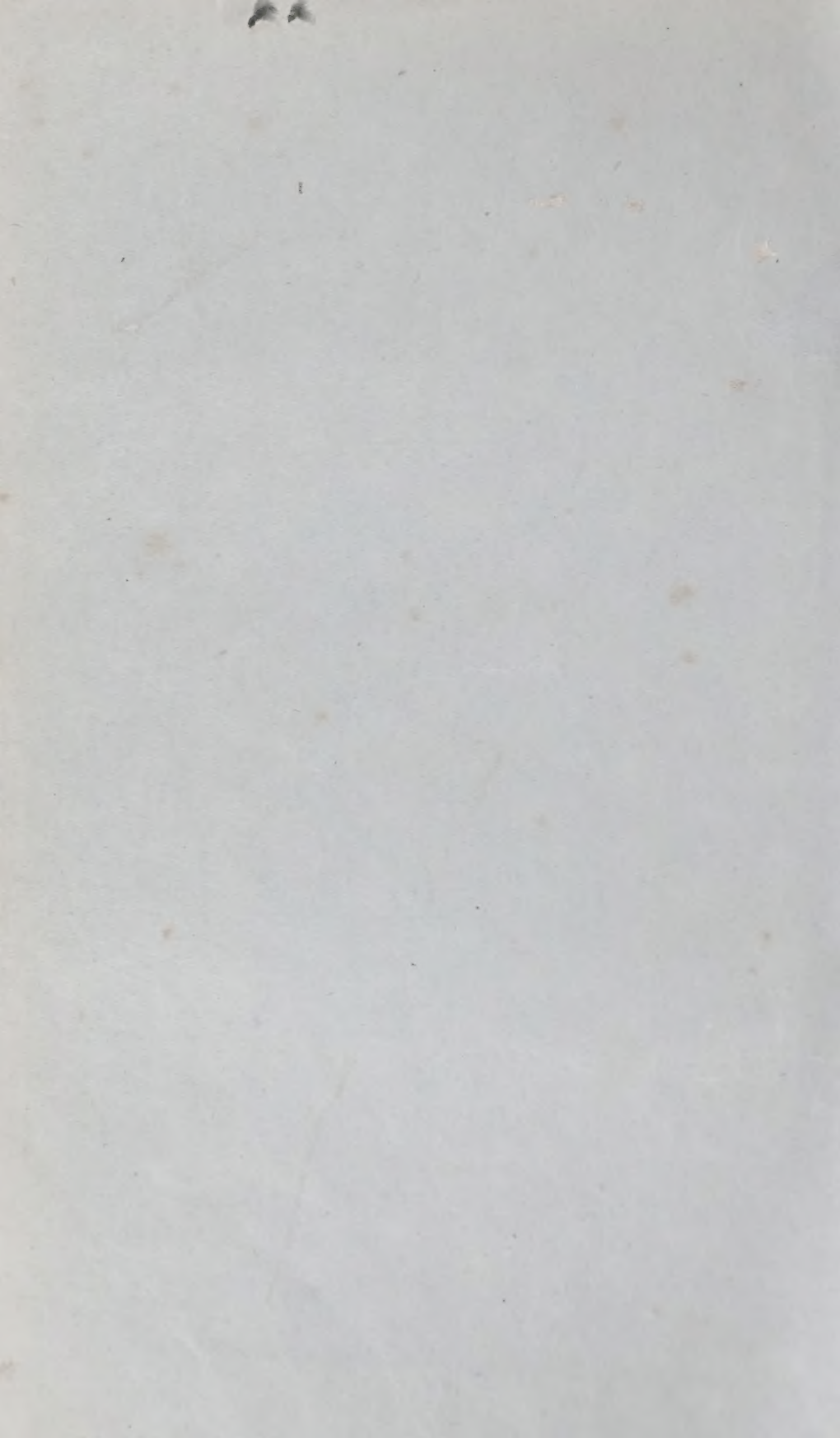
CFTRI-MYSORE



2396

Proceedings of t

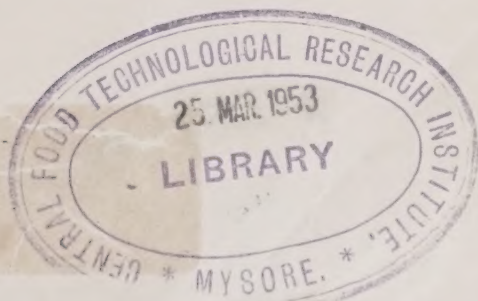
T Long





With the compliments of
Professor G. I. FINCH, F. R. S.,

Director,
National Chemical Laboratory of India,
POONA.

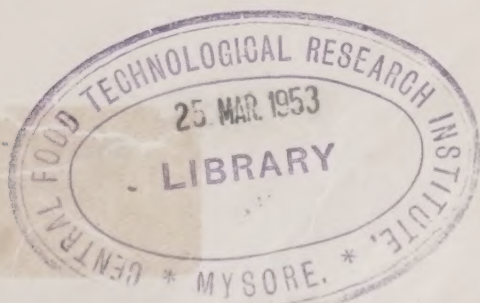


**PROCEEDINGS
OF THE
SYMPOSIUM
ON**

**INDIAN OILS AND FATS AND THEIR
UTILIZATION**

AT

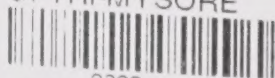
**THE NATIONAL CHEMICAL LABORATORY OF INDIA
POONA
1951**



2396/G.323

F-8, 4 up 2
W 51

CFTRI-MYSORE



2396

Proceedings of t.

ACKNOWLEDGMENTS

The Organiser of the Symposium records his grateful thanks to Dr. S. S. Bhatnagar, F. R. S., Director, Scientific and Industrial Research, New Delhi. and Prof. J. W. McBain, F. R. S., Director, National Chemical Laboratory, Poona, for their kind encouragement and guidance for the success of the Symposium.

He is also thankful to Mr. C. R. Mitra for his collaboration in compiling the manuscript and correction of the proofs.

The co-operation received from the other members of the National Chemical Laboratory in organizing the symposium is recorded with appreciation.

The authorities of the National Chemical Laboratory are thankful to the Indian Central Oilseeds Committee, Ministry of Agriculture, Government of India for a grant which ensured the publication of the complete proceedings of the symposium and making it available at a nominal price.

CONTENTS.

Page.

Acknowledgments	
Introduction	...
List of delegates who attended the Symposium	1
Opening Remarks BY Prof. J. W. McBain	3
Report of the 1st Symposium on 'Oil and Fats'	9
BY Dr. S. A. Saletore	...
	11
Scope of the Symposium: Oil and allied industries	
in India BY Dr. J. S. Aggarwal	...
	14

I. Oil Seeds and Vegetable Oils

Forest Oil-seed wealth of Bombay State	
BY I. M. Qureshi	...
	23
Gokhru (<i>Xanthium strumarium</i>) as a source of	
vegetable oil BY R. C. Shrivastava	...
	29
Kamala Seeds (<i>Mallotus philippinensis</i>) and its oil	
BY S. C. Gupta	...
	33
Utilization of Nim oil (<i>Melia indica</i>)	
BY Chittaranjan Mitra	...
	40
Utilization of Mowrah oil BY Dr. J. G. Kane	...
	55
Catastrophic increase in price of oils & oil-seeds	
BY T. V. Rao	...
	58
Oil and allied industries in the future development	
of India BY P. K. Patnaik	...
	64
Production and utilization of mustard oil in India	
BY Om Prakash	...
	69
Trading of vegetable oils in India and its future	
BY Tulsidas M. Vishram	...
	75
The refining of vegetable oils with special reference	
to Groundnut oil BY Krishan Gopal Mathur	...
	81
Rational utilization of oil-seed wealth of the country	
BY D. K. Gupta	...
	87

II. Oil Extraction

Nutan Ghani BY G. V. Datar	...
	95
The future of cottonseed oil milling and its	
utilization in India BY Dr. K. S. Murthi	...
	98
Prospects of oil milling industry in India	
BY Vallabhdas V. Mariwala, J. P.	...
	109
Practical working and economics of a modern	
solvent extraction plant BY H. V. Parekh	...
	114

The economic aspects of the solvent extraction process in the national planning of the Indian oil Industry BY Dr. N. G. Chatterji	...	118
Solvent extraction BY L. W. Richards	...	122
Availability of petroleum solvents for extration of vegetable oils BY T. K. Nayar	...	127
Extraction of Castor oil through aqueous medium BY J. P. Verma	...	130
Comments BY Dr. S. L. Sastry	...	132

III. Soap and Glycerine

The commercial and economic aspects of the Indian Soap industry BY Dr. Ing. B. P. Godrej	...	137
The use of non-edible oils in soap making in India BY G. Ford and Dr. G. S. Hattiangdi	...	141
Use of cheap commercial oils in making soap BY Dr. N. N. Godbole	...	144
The sweating of soaps and their prevention BY Dr. N. N. Godbole	...	145
Refining of glycerine by ion exchange resins BY Dr. H. A. Shah	...	147

IV. Hydrogenation of Oils

The <i>Vanaspati</i> industry—A brief survey BY A. E. Shohet	...	153
The nutritive value of <i>Vanaspati</i> BY Dr. M. Damodaran	...	163
A study of catalyst in <i>Vanaspati</i> production BY D. D. Nanavati	...	169
High pressure technique for fat splitting and hydrogenation of fatty acids BY Dr. R. K. Trivedi	...	175

V. Fish Oils.

Shark liver oil industry in India BY S. M. Arsiwala	...	181
---	-----	-----

VI. Castor Oil, drying oils, Paints & Varnishes

Some investigations on hydroxy oils particularly castor BY Dr. K. T. Achaya and Dr. S. A. Saletore	...	187
Dehydration of castor oil by substituted sulphonic acids and their salts as catalysts BY Dr. K. K. Dole	...	192

Dehydration of castor oil BY M. A. Sivasamban, Dr. S. A. Saletore and Dr. S. H. Zaheer.	...	197
Prospects of synthetic oils in paints and varnishes BY R. K. Banerji	...	200
Drier effects on drying of oil films BY Dr. S. A. Saletore, A. Hai and V. R. Harwalkar	...	202
Tobacco seed oil as a potential raw material in surface coatings BY P. Gopal Sharma	...	207
Utilization of vegetable oils for the preparation of alkyd resins from tetra-chlorophthalic anhydride BY Dr. D. J. Mehta	...	210
Cashew nut shell liquid—A potential raw material for the paints and varnish industry BY H. H. Mathur	...	212
Use of vegetable oils in the manufacture of modified alkyd resins BY Om Prakash	...	217

VII. Analytical and other Miscellaneous papers

Estimation of A & B values and the <u>butyro-</u> <u>refractometer</u> value in the evaluation of the purity of <u>ghee</u> BY Dr. N. N. Godbole	...	225
Recent advances in the analysis of oils and <u>fats</u> BY Dr. S. S. Gupta	...	227
Low temperature crystallisation technique BY Dr. C. B. Patel	...	231
Some recent advances in the study of the natural fats BY Dr. A. R. S. Kartha	...	236
Chromatography in the analysis of fatty oils and fatty acids BY V. S. Govindarajan	...	242
Stabilisation of edible fats BY S. C. Sethi	...	248
Estimation of acetyl value in determining the <u>rancidity of oils and fats</u> BY Dr. N. N. Godbole	...	253
Application of electrical testing methods in the processing of oils BY Dr. B. R. Y. Iyengar	...	254
<u>Carilla seed oil gel</u> BY Dr. J. W. Airan	...	256
Vegetable oils as <u>petroleum products substitutes</u> BY Dr. Mohan Lal Khanna	...	258
Some regularities in the melting and solidifying points of mixtures of fully <u>saturated</u> <u>glycerides</u> with non-fully saturated glyceri- des and saturated with <u>unsaturated fatty</u> <u>acids</u> BY Dr. A. R. S. Kartha	...	265

INTRODUCTION

The importance of detailed discussion of the various problems for fuller utilization of the Oil and Fat resources of the country was being felt in the recent years, and the first symposium on 'Oils and Fats' was held at the Central Laboratories for Scientific and Industrial Research, Hyderabad (Deccan) from the 12th to the 18th August, 1950. The second of its series, designated as 'Indian Oils and Fats and their Utilization' was organised by the National Chemical Laboratory of India, Poona, from the 7th to the 9th November, 1951. Prof. J. W. McBain, F R. S., Director of the Laboratory and Chairman of the Vegetable Oils Committee of the *Council of Scientific and Industrial Research* (India) presided. Besides the staff of the N. C. L., 101 delegates consisting of scientists, businessmen and industrialists from various parts of the country took part in the deliberations of the symposium.

The morning and afternoon sessions took place at 10 A. M. to 1 P.M. and 3 P. M. to 5 P. M. respectively each day. Except for the afternoon session of the 7th November which was held under the Chairmanship of Dr. R. C. Shah, *Assistant Director*, National Chemical Laboratory, the rest of the proceedings were conducted by the Organiser of the symposium, Dr. J. S. Aggarwal, *In-charge*, Oils and Fats Section.

Besides a paper on 'Oil and allied industries in India' covering the scope of the symposium, 49 papers were read and discussed under the following seven sections :

- (i) Oil Seeds and Vegetable Oils ;
- (ii) Oil Extraction ;
- (iii) Soap and Glycerine ;
- (iv) Hydrogenation of Oils ;
- (v) Fish Oils ;
- (vi) Castor Oil, Drying Oils, Paints and Varnishes ;
- (vii) Analytical and other miscellaneous papers.

The full papers and the brief reports of the discussion that followed are given in the succeeding pages.

A group photograph of the delegates along with the staff of the National Chemical Laboratory was taken on the morning of the 7th November before the session started.

The delegates were entertained at tea in the evening of the first day by the Director at the National Chemical Laboratory cafeteria.

A meeting of the Vegetable Oils Committee of the C. S. I. R. was also held on the morning of the 8th November, over which Prof. McBain presided.

At the conclusion of the symposium, the Organiser thanked the delegates, many of whom had come from long distances to make the symposium a success. On behalf of the members of the National Chemical Laboratory, he assured them that they had learnt much from them and as it was always mutual, he expected, that they had also been benefitted. He also thanked the various Organisations such as the Oil Merchants' Chamber, Indian Paint Manufacturers Association, Paint Federation and Akhil Bharat Sarva Seva Sangh who had sent their representatives for the Symposium. He further thanked the members of the N. C. L. whose help and cooperation was always with him.

Dr. J. G. Kane and Mr. T. M. Vishram while expressing appreciation on the successful conclusion of the proceedings of the symposium, spoke briefly on the usefulness of such meetings.

It was tentatively decided that the next symposium on Oils and Fats would be held under the auspices of The Oil Merchants' Chamber at Bombay. An invitation had also been received from the Oil Technologists' Association, Kanpur.

LIST OF DELEGATES WHO ATTENDED THE SYMPOSIUM.

1. Dr. Achaya, K. T.; Central Laboratories for Scientific and Industrial Research, Hyderabad (Deccan).
2. Dr. Airen, J. W.; Professor of Chemistry, Wilson College, Bombay.
3. Mr. Aphale, N. R.; D. E. S. Technical Institute, Poona-4.
4. Mr. Arsiwala, S. M., Superintendent (Technology), Office of the Director of Fisheries, Bombay-2.
5. Prof. Badne, M. D., M. E. S. College, Poona.
6. Mr. Banerji, R. K.; Murarka Paints Works Ltd., Calcutta (Representative of Indian Paint Manufacturers Association).
7. Mr. Bharatia, N. S.; The Elephant Oil Mills Ltd. Bombay (Representative of Paint Federation, Calcutta).
8. Mr. Bhargava, K. P.; Manager, J. K. Oil Mills, Kanpur (U. P.)
9. Mr. Bhat, S. M.; The Amrut Oil Mills Ltd., Bombay.
10. Mr. Bhattacharya, A.; H. E. Factory, Kirkee.
11. Mr. Bhow, N. R.; Chemical Engineer, The Swastik Oil Mills Ltd., Bombay.
12. Mr. Chanda, D. H.; P. O. Shrirampur, Ahmednagar.
13. Mr. Chanda, P. H.; 949, Gunj Peth, Poona 2.
14. Mr. Chakravarty, B. M.; H. E. Factory, Kirkee,
15. Dr. Chatterji, N. G.; Hindusthan Development Corporation Ltd., Calcutta.
16. Mr. Chaudhari, R. R., Conservator of Forests, Poona.
17. Mr. Chauhan, D. J.; P. O. Shrirampur, Ahmednagar.
18. Mr. Chaulam, G. S.; 84, Agriculture College, Poona.

19. Mr. Chinchanikar, S. S.; 711, Sadashiv Peth, Poona.
20. Mr. Dangri, A. G.; Ranade Institute, Poona-4.
21. Mr. Dattane, P. D.; 413-C Kalbadevi, Bombay-2.
22. Mr. Desikachar, N.; Chief Research Chemist, Tata Oil Mills Co. Ltd., Tatapuram (S. India).
23. Mr. Deshpande, A. D.; H. E. Factory, Kirkee.
24. Mr. Dharod, S. R.; 119, New Chinchbunder, Bombay-9.
25. Dr. Dole, K.K.; Professor of Chemistry, Fergusson College, Poona-4.
26. Prof. Fernandes, F.; St. Xaviers College, Bombay.
27. Mr. Gadre, K. B.; 2842, Sadashiv Peth, Poona-2.
28. Mr. Ghelabhai, Premji; The Oil Merchants Chamber Ltd. Bombay.
29. Dr. Godbole, N. N.; Director of Industries and Commerce Rajasthan, Jaipur.
30. Mr. Godbole, P. K.; Chemical Dept., Fergusson College, Poona-4.
31. Dr. Ing. Godrej, B. P.; Director, Godrej Soaps Ltd. Bombay.
32. Mr. Gupta, D. K.; Supervisor, Oil pressing Dept., Akhil Bharat Sarva Seva Sangh, Gram Udyog Vibhag, Maganwadi, Wardha (M. P.).
33. Dr. Hattingadi, G. S.; Lever Bros. Ltd., Haji Bunder, Sewri, Bombay-15
34. Dr. Ichhapuria, M.B.; The Tata Oil Mills Ltd., Tatapuram. (S. India).
35. Dr. Jatkar, S. K. K.; University Professor of Chemistry, Poona-4.
36. Mr. Joshi, M. A.; Chemical Dept., Fergusson College Poona-4.
37. Dr. Kane, J. G.; Dept. of Chemical Technology, Bombay University, Matunga, Bombay.

38. Mr. Karaekar, S. D.; Medical Student, Poona.
39. Mr. Kavthekar, J. W.; H. E. Factory, Kirkee.
40. Mr. Krishnamurti, V.; Engine House Road, Ordnance Estate, Kirkee.
41. Dr. Kartha, A. R. S.; Chemistry Dept., Maharaja's College Ernakulam (S. India).
42. Mr. Karve, D. V.; 325, Sadashiv Peth, Poona.
43. Mr. Kelkar, B. W.; Lecturer, Fergusson College, Poona.
44. Mr. Kelkar, G. M.; Chemist Incharge, Village Industries Research Laboratory, Poona 5.
45. Mr. Kelkar, G. R.; M. E. S. College, Poona.
46. Mr. Keskar, V. R.; Fergusson College, Poona.
47. Mr. Krimbkar, N. K.; Director, The Deccan Fertilizers Co. Ltd.
48. Mr. Kulkarni, M. V.; Fergusson College, Poona-4
49. Mr. Kulkarni, P. S.; Fergusson College, Poona-4
50. Mr. Lalkaka, K. E.; The Tata Oil Mills Co. Ltd. Sewri, Bombay.
51. Mr. Lele, A. M.; Village Industries Research Laboratory, Poona 5.
52. Dr. Magar, N. G.; Royal Institute of Science, Bombay.
53. Mr. Makwana, I. M.; 949, Gunj Peth, Poona-2.
54. Dr. Mandlekar, M. R.; Deputy Director of Industries, Bombay.
55. Mr. Mariwala, Valabhadas V.; Vice President, The Oil Merchants Chamber Ltd., Bombay.
56. Mr. Mathew, B. N.; Ranade Institute, Poona-4.
57. Mr. Mathur, Krishna Gopal; Chief Chemist, Kusum Products Ltd., P. O. Rishra, West Bengal.
58. Dr. Murthi, K. S.; Director, Oil Technological Institute, Anantpur, (Madras State).

59. Dr. Muzumdar, G. G.; Director, Research Laboratory,
Aurvedic Mahavidhyala, 22, Nangesh Peth, Poona-2.
60. Mr. Narasimhan, K. R. L.; Addison Paints and Chemical
Ltd., Huzur Gardens, Madras.
61. Mr. Nayar, T. K.; Representative, Burma Shell, Poona.
62. Mr. Pabane, J. S.; St. Xaviers College, Bombay.
63. Mr. Parekh, H. V.; Chemical Engineer, The Bhavnagar,
Chemical Works (1946) Ltd., Vartej (Saurashtra).
64. Dr. Patel. C. S.; Dean of Faculty of Science, M. S. Uni-
versity of Baroda, Baroda.
65. Mr. Patil, K. K.; Research Student, Fergusson College,
Poona-4.
66. Mr. Patnaik, P. K.; Special Officer, Oil Co-operatives,
Govt. of Orissa, Bhuvaneshwar.
67. Mr. Patkar., J. D.; The Bassein Paints and Varnish Co.
Ltd., Bombay.
68. Mr. Pendse M. S.; 200/5 Sadashiv Peth, Poona 4.
69. Mr. P. Ingle, S. V.; Fergusson College, Poona 4.
70. Mr. Prakash, Om, Oil Expert to Uttar Pradesh Govt.,
H. B. T. I., Kanpur.
71. Mr. Qureshi, I. M.; Silviculturist, Bombay State, Poona-1.
72. Mr. Rai, Haridaman; Govt. Trainee, H. E. Factory, Kirkee.
73. Mr. Rao, C. R.; General Manager, The Tata Chemicals
Ltd., Bombay.
74. Mr. Rao, V. T.; C/o Dr. Janardana Rao, Retd. Civil
Surgeon, Mangalore.
75. Mr. Raghavan, R. V.; Joint Editor, Paintindia, Bombay.
76. Dr. Rathi, R. J.; 614-Raviwar Peth, Poona-2.
77. Dr. Raysarkar, B. C.; Defence Science Organisation, Govt..
of India, New Delhi.
78. Mr. Reddy, U. R.; Bhavsinji Polytechnic, Bhavnagar,
(Saurashtra).

79. Mr. Ribeiro, D. J.; Chemist, B. S. Forest Laboratory,
Dharwar (Bombay State).
80. Mr. Ruparth, T. H.; 85, Agriculture College. Poona.
81. Dr. Saletore, S. A.; Assistant Director, Central Laboratories,
for Scientific and Industrial Research, Hyderabad (Dn).
82. Mr. Sane, J. J.; 84, Kazisyed Street, Bombay-3,
83. Mr. Saraf, V. A.; Fergusson College, Poona-4.
84. Mr. Satyanarayanan, M. B.; Addison Paints and Chemicals
Ltd., Huzur Gardens, Madras.
85. Mr. Sawala, R. L.; 3-Chinchbunder, Bombay-9.
86. Mr. Sethuraman, S. G.; Joint Editor, Paintindia, Bombay.
87. Mr. Shah, P. G.; 3, Chinchbunder, Bombay-9.
88. Mr. Sheth, R. C.; Editor, Oil and Oil-seeds Journal,
Bombay.
89. Mr. Shohet, A. E.; The Hindustan Vanaspati Manufactur-
ing Co. Ltd., Bombay.
90. Mr. Shokkar, Naranji H.; Vasanji Mulji & Co., Dongri
Street, Bombay 9.
91. Mr. Shrivastava, R. C.; Agricultural Chemist to Govt.
Madhya Pradesh, Nagpur (M. P.).
92. Mr. Singh, G. S.; Chief Conservator of Forests, Bombay.
State, Poona-1.
93. Mr. Sivasamban, M. A.; Central Laboratories for Scientific
and Industrial Research, Hyderabad (Dn.)
94. Mr. Subbarao, T. V.; Tata Oil Mills Co. Ltd., Tatapuram.
(S. India).
95. Mr. Tanna, J. J.; The Oil merchants Chamber Ltd.,
Bombay.
96. Mr. Thakkar, N. H.; The Oil Merchants Chamber Ltd.
Bombay.
97. Dr. Trivedi, R. K.; C/o Itraco Ltd., 339, Hornby Road,
Bombay 1.

98. Mr. Vishram, T. M.; Hon. Secretary, The Oil Merchants Chamber Ltd., Bombay.
99. Mr. Wagadhnkar, V. D.; H. E. Factory, Kirkee.
100. Mr. Zacharissen, B.; Representative, De Laval Industries, Bombay.
101. Mr. Zahna, B.; S. K. F. Bombay.

OPENING REMARKS By Prof. J. W. McBAIN

It is my privilege to welcome you here to this symposium on a subject of great importance to India. Some of you are here for the first time, although many are old friends. I say old friends, although National Chemical Laboratory is still in its infancy. I hope you will take interest in this laboratory because it is yours. It is a public service institution and is at your service. You are welcome to give your suggestions and thus help the country and yourselves. Now some of you have not yet had the opportunity of seeing the laboratories. You just see the central part, it looks like a country club, and is situated in a beautiful place. The library is important. In the first floor, second floor and ground floor the work is going on. In the east basement, is the well equipped Physical Chemistry Division; in the west basement, we have the Chemical Engineering and the Workshop. You would perhaps like to see as much as you can of the work of the Laboratory.

Unfortunately the Export Committee had to hold their meeting on the 6th at Madras and people who had expressed their intention of coming over here couldn't come. More are expected during the next two days.

This symposium is one of a series of symposia that we have been holding on an average of one a month, covering the most important phases of Chemistry and Chemical Industry. A very important was on basic chemical industry. I wish all were more aware of the necessity for having a complete integrated basic chemical industry, upon which we can build the remaining other chemical industries, and also support the other industries that are essentially dependent upon basic chemicals.

Last year the symposium on *oils and fats* was held at Hyderabad and I am to request Dr. Saletore to make an announcement in that connection.

The object of the symposia is to bring together Government officials, industrialists, scientists and University men to exchange information and learn each other's view points. Incidentally, the National Chemical Laboratory, is accumulating a liberal education by having the opportunity of meeting all you distinguished people, the leading people in each of the subjects of the different symposia.

The next symposium is to be on "The Utilization of industrial Wastes." As you may understand, it is quite an important problem. The organiser of the Symposium was one of those who was fortunately deputed to go to the United States for an extended tour at the expense of the Ford Foundation. February 13th to 15th has been fixed as the date for this symposium. We hope all those interested will take part and profit from the symposium.

Now, a record is being kept of the proceedings of this symposium, as has been done in the preceeding symposia. A wire recorder is here which takes down every word said on the microphone. We have stenographers, and we also request all speakers to hand over their manuscripts to the Secretary of the symposium. From the manuscripts as well as the stenographic notes, we get the full proceedings. This permanent record will be distributed to you. All those who want to receive this may please leave their names and addresses with the Receptionist.

With these few words, I trust and fully expect that this will be a very successful symposium. The very interesting papers that you are offering are as good as could be offered in any country in the world. The only trouble is shortness of time for adequate treatment and discussion. This may be made up by the permanent record to which I referred.

I fully expect that the personal talks and the discussion of papers presented here will be important, and lead to considerable advances in the subject of Oils and Fats, in which we are all interested, and which is one of the country's great natural resources that need still further development.

I now ask Dr. J. S. Aggarwal to take the chair.

REPORT OF THE 1st SYMPOSIUM ON OILS & FATS

BY

Dr. S. A. SALETORE.

*Central Laboratories for Scientific & Industrial Research,
Hyderabad (Deccan).*

The first symposium on *Oils and Fats* was held under the auspices of the Central Laboratories for Scientific and Industrial Research, Hyderabad (Deccan) from the 12th to the 18th August, 1950, concurrently with two other symposia on *Fuels* and on *Research & Industry*. As Sir J. C. Ghosh, who was to have inaugurated the proceedings, could not attend due to illness, he sent us his written address. Dr. S. Husain Zaheer, Director of the Central Laboratories, in a welcoming speech hoped that the idea of such symposia would catch on, and stressed their numerous advantages—contacts, co-operative efforts, counteracting tendencies against overlapping, and stimulus to workers themselves. Messages of good wishes from various scientists were read, and some of the guests present also spoke briefly expressing their pleasure at being with the delegates. The Presidents for the three series of symposia were named—Dr. S. A. Saletore—*Oils and Fats*; Dr. H. G. Kayser—*Fuels*; and Dr. B. S. Kulkarni—*Research and Industry*.

In the *Oils and Fats* Symposium, seven papers were presented during the next few days each followed by a vigorous, but friendly and informal discussion. Dr. S. A. Saletore presented the first paper entitled “ *The Future of the Edible Fat Industries in India* ”. Giving facts and figures, he pointed out the serious nature of the shortage of edible fats in this country, with the present consumption around 1.23 million tons. In order to raise the *per capita* figures from 0.34 oz. per day to a minimum requirement of 2 ozs. per head, an additional 3.65 million tons per annum are required and he suggested how this could be met with by different methods, including utilization of cotton seed oil, hydrogenation of linseed oil and a greater use of non-edible oils in industry to liberate edible oils for edible purposes. He referred to the indispensibility of oil *ghanies* and suggested modernising the same and spoke on the failure of solvent plants erected in this country and stressed the need for more careful consideration of plant design and suitability for Indian conditions if future failures are to be averted. As regards *vanaspathi* it was necessary to realise its good as

well as bad points; the industry itself was to be blamed for its present plight and if *vanaspati* were sold on its own merits which were perfectly sound, it had a bright future.

Finally, he made brief mention of the need for research on the merits of different oils for cooking different types of food products, and appealed for more attention to problems outside the beaten track. The ensuing discussion centred on yeast fat as a supplementary food source, on solvent extraction and on grading of oilseeds.

Dr. J. S. Aggarwal next spoke on *Castor Oil and its Gel* : He briefly described the habitat and varieties of the castor plant and the characteristics, grades and uses of its oil, mainly as Turkey red oil and lubricant oils. The heat treatment of castor oil was then discussed, mention being made of dehydration and its subsequent developments, and of the heating of alkaline castor soaps to give alcohol and dibasic acid. Dr. Aggarwal then described his work on the utilisation of the gel obtained by heating dehydrated castor oil : on careful steam treatment this gave a product (mixed dimer and monomers), the salts of which could be used with linseed oil as excellent varnishes. The discussion that followed dealt largely with the process of dehydration of castor oil and the analytical methods involved.

The Utilization of Tobacco seed, Safflower and like oils as Surface Coating Materials was the next paper, presented by Dr. J. S. Aggarwal. Linoleic acid rich oils abounded in India, and tobacco seed oil and safflower oil represented two such : both yielded blown and polymerised oils of excellent quality, giving efficient coating materials. The mechanism of blowing was then described, and this was continued in the discussion that followed, where the edibility and economics of the two seed oils were also gone into.

Prof. B. N. Banerjee followed with a talk on *Nutrition* with respects to fats. He particularly stressed the importance of the fats as carriers of vitamins and carotene, and dealt with the factors involved in storage stability of the same, seed storage conditions, free acidity, fat composition and natural and synthetic anti-oxidants. He showed that the breakdown products which sterols produced on storage were pro-oxidant. During the ensuing discussion controversial views on the digestibility of different fats were presented.

Rancidity of Vegetable Oils was the title of the next paper by Dr. S. A. Saletore, who stressed the fact that while the main characteristic of rancidity was its smell, nearly all the theories and

methods dealing with the same were based on atmospheric oxidation giving rise to non-odorous products. Experimentally he had found a considerable lack of correlation between organoleptic smell and auto-oxidative changes, and so in his opinion it was necessary to look for changes other than the accepted ones based on oxidation to explain the phenomenon of rancidity. Based on results obtained by him, he put forward the interesting idea that possibly nitrogen fixation by the oil may have something to do with it.

Various suggestions for further work on the subject were made during the discussion and the question of smell measurement of same touched upon.

Mr. H. H. Mathur presented the next paper on *Rosin in Varnish and Soap Industry* indicating the composition and chemical properties of rosin, and its various derivatives; ester gum and lime-hardened rosin, pentaerythritol and glycerol esters, and his own formulations using maleic acid, cashew and bhilawan shell liquids, and polyfunctional alcohols. A wide field was covered in the discussion that followed.

Dr. K. T. Achaya presented the last paper on *Fats in Dairy Industry* tracing the many interesting physico-chemical transformations that the fat of milk undergoes during its conversion into *ghee*. He referred to the fat globule membrane, to carotene and vitamin A secretion theories, to the stability conferred on heating butter into *ghee*, the large scale manufacture of *ghee*. Sundry dairy problems were discussed following the lecture: the yields of milk and *ghee* from Indian cattle, goat breeding and the physiology of fats.

Before the session ended Dr. S. A. Saletore referred to a topic which was uppermost in the minds of a number of oil chemists and Technologists in India, viz. the need for a truly representative All India Association and high class Journal for oils. After a number of speakers had spoken on the subject, Dr. Saletore was asked to draw up a scheme on the basis of the suggestions put forward at the meeting, discuss same with those in charge of the Kanpur Association, and bring up the matter again during the Science Congress to be held at Bangalore.

Two excursions were arranged during the symposia: one to the historical Fort of Golconda, Osmansagar lake and the old city of Hyderabad; and another to various factories and institutions around Hyderabad city. The proceedings of the Symposium have been published, and copies are available for sale.

SCOPE OF THE SYMPOSIUM : OIL AND ALLIED INDUSTRIES IN INDIA.

BY

DR. J. S. AGGARWAL,

National Chemical Laboratory, Poona.

In order to consider the scope of this symposium it is necessary to discuss the present position of oil and allied industries in India and to find out the ways and means by which such industries can further be developed in this country.

India is not only one of the leading oil-seed producing countries of the world, but is perhaps the only country, which produces in commercial quantities greater variety of oil seeds than any other country. With the exception of palm kernel, olives, soybeans and tung, she produces all the principal oil seeds which form the basis of the world's oil seed crushing industry. About 8 per cent of the total area under cultivation is devoted to the production of oil bearing crops and she contributes about 20 per cent of the world's production of oil seeds.

The production of principal oil-seeds in India as compared to that of the world in 1948-49 was groundnut 62 per cent, cotton seed 25 per cent, rape and mustard 15 per cent, sesame 26.8 per cent, linseed 15 per cent, castor seed 29 per cent, copra 5.8 per cent and in mahua seed India holds a monopoly. It is interesting to mention here that a potential substitute of Tung or Chinese wood oil has also been found in this country. This is *Kamala* Oil obtained from the seeds of a plant, *Mallotus Philippinensis*, belonging to the Natural Order *Euphorbiaceae*.

India is perhaps the only country in the world which can produce fat which is almost pure tri-laurin. This fat is obtained from *Pisa* seeds the plants of which grow in the forests of Bombay and Madras States. The superiority of lauric and myristic acid soaps over other fatty acid soaps as regards detergency, hardness, and solubility in water is well known and if this seed fat be made available in large quantities, it may entirely replace the coconut oil in soap-manufacture.

With such a large production of oil seeds in this country it is natural to expect that various industries whose major raw materials are oils and fats must develop in India. This has actually been the case. The oil seed crushing, soap and glycerine, paint and varnish and *vanaspati* industries are very important industries of this country. India is almost self sufficient with regard to these commodities.

Taking the oilseed crushing industry, although bullock driven *ghanies* were being employed in India from time immemorial, large scale crushing of oil seeds with modern appliances does not appear to have been started until after the close of the first World War. Till that time large quantities of the oil seeds produced in the country such as copra, castor, groundnut, linseed and sesame used to be exported out of India. The second World War gave a further impetus to the oil seed crushing industry with the result that the bulk of the oil seeds produced are now crushed within the country. It has been roughly estimated that there are (1) about four lac bullock driven *kohlus* crushing annually about seven lac tons of oil-seeds of different varieties and (2) a large number of small oil mills having in all about 8,500 power driven rotary *ghanies* and 50 screw presses crushing about six lac tons of oil seeds per annum. There are about 1,000 big oil mills in the country having 3,000 expellers, 100 hydraulic presses and 15,000 power driven *ghanies* which crush about twenty five lac tons of oil seeds per annum. A 50 ton solvent extraction plant has also recently been installed at Bhavnagar Chemical Works (1946) Ltd., Vartej (Saurashtra). It mostly extracts residual oil from pressed groundnut cake. Another 30 ton solvent extraction plant is being erected at Porbandar (Saurashtra).

The soap and glycerine industry got special incentive from the *Swadeshi* movement in 1930. From that time the production of soap went on increasing in the country and the import correspondingly declined; so much so that in 1944 India produced 1,40,000 tons of soap of which about 10 per cent was milled toilet soap. In 1947-48 India imported only 517.3 tons of soap which was mostly of medicinal variety. A modest beginning has also been made in the export trade of this commodity and in 1946-47 India exported 2037.5 tons of soap to Middle East, Far East and African Countries. About 3,000 tons of glycerine is also produced annually in the country.

Paints and varnishes are another important industry in which oils form an essential raw material. This industry only developed after the first World War. Paints and other coating compositions of the value of about six crores are being consumed annually in the

country. The number of paint and varnish factories in India at present is reported to be about 150. The capital invested in the industry is about 2.7 crores. The output of paints and enamels in 1949 was 30,929 tons. The import of paints and enamels in 1949 dwindled to 1642 tons as against 6,000 tons in 1937-38. Linseed oil is the main drying oil that is used in the production of various coating compositions although a very small amount of Tung oil and dehydrated castor oil are also now being employed. Tung oil is in very short supply. The importance of the development of Kamala oil as a substitute for Tung oil has been mentioned already. As regards pigments : projects for the production of Titanium dioxide and aluminium pigments are under way. India, however, still imports lithopone, titanium dioxide, carbon black, aluminium paste and powder, ultramarine blue, pigment dyes, copal gum and synthetic resins, etc. We do not yet produce some of the volatile organic solvents.

The *vanaspati* or the vegetable product industry came into being only in 1930. India imported 22,909 tons of hydrogenated fat in 1928-29. The production of *vanaspati* has, however, increased so rapidly in this country that in 1949, 152,728 tons of *vanaspati* was manufactured in the country and there was absolutely no import. At present there are about 42 *vanaspati* factories in India with a total production capacity of about 3,21,000 tons per annum. Besides the existing factories there are 17 more which are either under erection or for which licences have been granted by the Government of India. Since 1946, India is also exporting *vanaspati* to a small extent.

Taking the manufacture of machinery for oil and allied industries, production of ordinary types of machinery such as heating pans, storage tanks, filter presses, etc., has been started during the last few decades. Rotary *ghanies* are commonly manufactured in various places in India. Further modifications of village *ghanies* have resulted in the development of Wardha and Nutan Ghanies. Simple types of soap equipment, such as boiling pans, cooling frames, soap cutting and stamping machines are manufactured in the country by a number of firms. But the other equipment for oil and allied industries has not yet been developed in India. Equipment like Anglo-American presses, cage presses, seed crushing rolls, reduction rolls, seed decorticators, disintegrators, hydraulic pumps and accumulators are all still imported. Similar is the case with equipment for soap, paints, varnishes and hydrogenation.

Besides the existing industries there are other industries for which the major raw materials are oils and fats that may be developed

in this country. Commercial stearic acid and other important fatty acids for the cosmetic and other industries are required in large amounts. Relston points out: "The use of fatty acids as starting materials in chemical synthesis is still, however, largely unexplored, and provides greater opportunities than any other field, for the combined efforts of research chemist and chemical engineer. Chemical intermediates and industrial chemicals made from fatty acids include nitriles, aliphatic amines, fatty alcohols, wax-like dialkyl ketones and aryl alkyl ketones are useful plasticisers, waxes, coating compounds, paint bases and lacquer substitutes." The products from Kamala oil show possibilities of many types of utilizations. The compounds obtained by the cracking of castor oil and its soap, such as sebacic acid, octyl alcohol, undecylenic acid and heptaldehyde are useful for plastics, plasticizers and for perfumery formulations. It is, therefore, necessary that the production of such compounds from various fats and oils may be started in the country.

India produces only a very small quantity of mineral oil and she has to import her requirements for lubricating oils mostly from abroad. The work carried out in the laboratories of the Council of Scientific and Industrial Research and at other places in India have definitely shown that many vegetable oils after suitable modifications can be used for various types of lubricants. Moreover, the major components of lubricating greases are the metallic salts of various fatty acids. Vegetable lubricating oils and grease industry may, therefore, have a great prospect in India. The modern jet planes are entirely dependent for flight, upon castor oil from which the multipurpose lithium greases are made.

Besides the above there are other industries where oils and fats and their products are raw materials to a greater or less extent, such are textiles, rubber tyres, ointments, polishes, leather articles, hydraulic brake fluid, typewriter ribbons, disinfectants, linoleum, printing inks, etc.

With the growth of oil and allied industries in India the export of oil seeds has substantially gone down. The export of oils and oil seeds amounted to only about 2 lac tons in 1948-49 while during the prewar period it averaged about 8 to 10 lac tons, the bulk of the production being required for home consumption. In spite of it, there is a shortage of oils and fats in the country which can be realised from the fact that the *per capita* per day consumption of oils and fats in India works out to about $\frac{1}{2}$ oz., whereas only for edible purpose, the minimum *per capita* per day consumption of fats, as recommended by

the Nutrition Advisory Committee is about 2 oz. The prices, especially of edible fats, are rapidly increasing in the country. Increased industrial activities like the development in the paint and soap industries, increase in population and the prohibitive price of *ghee* have caused a heavy drain on the vegetable oils. Again, much of the acreage formerly under oil seeds has been of necessity switched on to food crops.

It is, therefore, necessary to find out methods for removing the present shortage of oils and fats so that after adequately satisfying her own requirements, India may be a good exporter of these high priced cash crops. One of the solutions is to increase the overall output and the yield per acre either by intensive or extensive measures or by both. The establishment of the Indian Central Oil Seeds Committee in 1947 marked an important landmark in the history of oil seeds in India. Since then research work has been extended and it is expected that in the coming years the yield of the principal oil seed crops in the country will record an appreciable increase. Satisfactory progress has been made at Madras, particularly in regard to groundnut. Considerable spade work is reported to have been done in Hyderabad since that state accounts for nearly 50 per cent of the castor seed production in the Indian Union.

Then there are oil seeds which grow in large amounts but are not entirely and properly collected. Some of them are rich sources of oils. *Nim* seeds and tobacco seeds are the most glaring examples. The availability and utility of these seed oils will form subjects of two subsequent papers in the Symposium. Vegetables and fruits like pumpkin, melon and water melon are consumed when the seeds are absolutely ripe. The seeds are mostly thrown away. Some scheme should be adopted to collect all these seeds as they contain considerable amounts of edible oils. There are less known oil seeds like *Kamala*, *Pisa* fat, *Phulwara* butter, *Khakan* fat, *Argemone*, and *Moringa* seeds, the yields of which when increased by extensive plantations and improved collection methods can form rich sources of important oils and fats. These seed oils can be used in various industries. This will relieve to a great extent the strain on edible oils which are at present mostly used for these purposes.

For further increasing the amounts of seed oils, the solvent extraction method should be adopted in the country, as soon as possible. Five to ten per cent of oil that always remains in pressed oil cakes goes as waste. Then there are oil seeds known which contain less than 20% oil. The economic extraction of the oil from such seeds may only be possible by solvent extraction process. The non-availability of the

solvents is the greatest handicap for the employment of the solvent extraction process in this country. Petroleum solvents are produced in very small amounts. It is necessary, therefore, that the production of benzene and chlorinated solvents should be increased. The raw materials for these solvents are available in the country. The new method of aqueous extraction of oil from oil seeds developed in the National Chemical Laboratory of India, Poona may have a bright future in this country.

The other methods of increasing our output of fats and oils is by developing the fish oil industry. Shark liver oil is being obtained in India at the present time and it is mostly used for pharmaceutical purposes. If the production of this oil and other fish oils is increased they may form a good raw material for various coating compositions.

Lastly, but not the least important, is the need for development of a flourishing dairy industry in India. There is a vast scope for this industry to thrive side by side with the *Vanaspati* industry. Butter and *ghee* if available at reasonable prices will certainly be used in preference to *Vanaspati* and other edible fats.

OIL SEEDS
&
VEGETABLE
OILS

FOREST OIL SEED WEALTH OF BOMBAY STATE

BY

I. M. QURESHI

Silviculturist, Bombay State, Poona.

Introduction.

It may perhaps be not wrong to say that though India ranks first in the world in production of oil seeds of agricultural produce like ground nut, til, safflower or kardi, linseed, coconut, castor etc., very little attention appears to have been paid to the survey, assessment, organisation, utilisation, and marketing of the forest oil-seed wealth of the country, particularly of the non-edible types which in quite a number of cases hold bright prospects not only in substituting the costly imported produce but also in supplementing the industrial demands in soapmaking, paints and varnishes etc. Examples may be cited of Kamala (*Mellotus philippinesis*), Mohawa (*Bassia latifolia*), Pissa (*Actinodaphne hookeri*), Karanj (*Pongamia glabra*). Nim (*Azadirachta indica*) etc. Some of them are of great medicinal value too, such as *Hydnocarpus Wightiana* (the substitute for chaulmogra oil), *Schleichera trijuga*, *Bixa Orellana* (for "Arnatto" dye) etc. It may be mentioned that according to Puran Singh (Indian Forester No. 6, 1913) the percentage of oil in the kernels of *Schleichera trijuga* vary from 57 to 80 and the oil contains small quantities of hydrocyanic acid probably generated by the action of an enzyme on a cyanogenic glucoside in the seed. It has been tried for soap with success and what is more valuable is that it has very beneficial effect on the growth of the hair. Puran Singh considers this oil to be worthy of forming the base of all hair oils and in fact is the base of the well known *Mecassar* oil.

While problems of sustained yield, regular supplies and economic collection are the governing factors of any commercial enterprise, it is worth considering how best to augment the natural growth of important oil-yielding species by artificial plantations, conservation of existing stocking and organising collection on some co-operative or cottage industry basis. I, therefore, propose to merely list up some of the more important forest oil-seeds of Bombay State.

Oil yielding species.

In a general sense, majority of the albuminous seeds are rich in oil contents and whatever our present day knowledge is, it is

regarding those species which have been so far investigated. As Forest Officers, we have a rule of thumb based on experience that those seeds which lose viability and give low percentage of germination after some storage are indicators of oil wealth e. g. Mohawa, butter tree, Kamala etc. It, therefore, stands to reason that there be many unknown seeds which may be rich in oil. A recent example of such a class is the thin papery, winged seed of *Holoptelea integrifolia* (Urticaceae), which till the time I requested Dr. J. S. Aggarwal to analyse was perhaps not known to yield as much as 50 per cent of a fine quality, pale yellow oil which can even be made as edible as coconut oil with little deodorisation. A small bag of such seed was supplied by me to Dr. Aggarwal with a request to analyse it and Dr. Aggarwal here may tell you about his findings. The tree seeds profusely annually and occurs in many parts of India in deciduous forests.

There is a wide field and immense scope for investigations on the utilisation etc. of the forest oil-seeds. To mention a few, the following 38 species may be listed and on which a considerable amount of work has been already done by various research workers.

1. *Actionodaphne Hookeri*—(*Pissa*)

This is a well known seed which contains as much as 50% of fat and may prove to be a good dollar-earner in other countries. In fact, there was recently a query from the High Commissioner for India in London regarding the total quantities annually available in various parts. In Bombay State, it occurs mostly in Mahabaleshwar and to some extent in Lonavla, Khandala, Matheran and Kanara forests. The total yield from Central Circle is estimated to be 250 Bengal maunds but the difficulty is regarding collection which falls in a season when local villagers are busy with agricultural operations.

2. *Aegle Marmelos* (*Bael fruits*).

A sacred tree occurring in dry forests throughout India. The oil percentage is 44.1 in the kernel.

3. *Azadirachta indica* (*Neem*).

A very rough estimate of the yield is about 8000 Bengal maunds per annum. The species is also annually extended by artificial plantations in dry areas.

4. *Anacardium occidentale* (*Kaju*).

Occurs in coastal tracts and is well-known for its shell oil and edible fruits.

5. *Ballanites Roxburghii* (Hinganbet).

Kernels yield 48 per cent oil; occurs scattered in dry deciduous forests.

6. *Bassia latifolia* (Mokawa).

Information supplied by the Forest Utilisation Officer indicates possibilities of as much as 15,000 Bengal maunds per annum.

7. *Bassia longifolia*.

This occurs in limited quantities.

8. *Bassia butyracea* (Butter tree of Almora & Kumaon hills).

Plantations of this are being raised on an experimental scale in suitable parts of the State.

9. *Bixa orellana* (Arnotto).

Occurs very sparsely.

10. *Bombax malabaricum* (Silk cotton).

The seeds has 29.72 per cent of oil. The tree occurs throughout India in deciduous forests.

11. *Buchanania latifolia* (charoli).

It occurs throughout India - in Bombay State, mostly in deciduous forests as those of Khandesh etc. The oil in kernels varies from 60 to 67 per cent and the percentage of kernels in the total seed varies from 19 to 23 per cent. The seed kernel is sold in the market as "charoli" or "chironji" which is used as dry fruit in manufacture of sweets etc.

12. *Butea frondosa* (Flame of the forest or Palas).

Occurs throughout India in dry forests. The oil in total seeds amounts to 22.52 per cent.

13. *Callophyllum inophyllum* (Undi).

Occurs in coastal tracts of W. D. Kanara and oil is used for burning and soap making.

14. *Cossia fistule* (The Indian Laburnum or Amaltas).

Occurs scattered throughout India in deciduous forests. It gives 56.26 per cent of oil in the kernels.

15. *Celastrus paniculata*.

Talbot records that a large quantity of fruits of this species are brought into Belgaum market during the months of July and August. The oil in seeds varies from 55.3 to 77.3 per cent and is a dark red pungent oil which is said to be a nerve tonic and applied externally to sores.

16. *Cochlospermum gossypium*.

Occurs in many parts of India. The oil in the total seeds varies from 13.3 to 17.5 per cent.

17. *Chloroxylon swietenia* (*Satinwood tree*).

The seed was supplied to Mr. J. N. Marshall, Bombay, who reported that the yield of oil in kernel is 16.5 per cent. It is typical semi-drying vegetable oil which could be put to a number of uses. About 153 maunds of seed is available in Southern Circle of Bombay State (Gokak, Gujnal, Kod, Badami, Bagalkot etc. Ranges).

18. *Dispyros montana*.

Kernel gives 22.3 per cent of oil and occurs in parts of Southern Circle.

19. *Garcinia Cambogia* (*Dharambi*).

Occurs in semi-evergreen and evergreen forests of Southern Circle. It is the camboge butter tree.

20. *Heynea trijuga*.

Occurs scattered in dry and moist deciduous forests in many parts. Kernels give 37.45 per cent of oil.

21. *Holoptelea integrifolia*.

The seed has been supplied recently to the National Chemical Laboratory of India, and may contain over 50 per cent of oil in the kernel.

22. *Hydnocarpus Wightiana*.

Occurs scattered in parts of Southern Circle in semi-evergreen and evergreen belt. Oil in kernel is found to be 60.7 per cent and is used as a substitute for the famous Chaulmugra oil.

23. *Mallotus philippinensis* (*Kamala*).

Occurs scattered in moist deciduous forests as an undergrowth or a small tree. Recent survey gave a conservative figure of about 1500 lbs. though there are indications of a much higher yield. It is

a worthy substitute of the Tung oil. It contains about 50 per cent of oil in the kernels. Large quantities of seeds have already been supplied for tests to the National Chemical Laboratory of India by this Office in the past.

24. *Mesua ferrea* (*Nagchampa*).

Occurs scattered in evergreen forests of Kanara. Gives a dark coloured oil used in medicine and for burning, the yield being 73-76 per cent.

25. *Mimusops Elengi* (*Bakul or Molsari*).

Occurs in evergreen forests of Kanara. The oil contents is about 23.3 per cent.

26. *Mimusops hexandra* (*Khirni*).

Occurs in dry parts of Khandesh, Gujerat etc. Oil in kernels is 46 per cent. The fruit is edible and sold in market as *Khirni*.

27. *Myritica attenuata* etc.

The species occurs in evergreen forests of Kanara. It is called " *Ran Javtri* ". The percentage of oil in kernels may be about 45 per cent as in case of *Myristica malabarica*.

28. *Phyllanthus Emblica* (*Amla*)

Oil in the kernels is 12.69 per cent. The tree occurs throughout India in deciduous forests.

29. *Salvadora oleoides* (*Khakan fat*):

The tree occurs in drier parts of North Gujerat on saline soils.

30. *Salvadora persica*.

It occurs mixed with *Salvadora oleoides* in above regions but occupies slightly more moist situations.

31. *Semecarpus anacardium* (*Bhilawan*).

Occurs throughout deciduous forests in India. The oil in kernels varies from 39.1 to 44.6 per cent.

32. *Schleichera trijuga* (*Kusum*).

Occurs scattered in comparatively moist situations in moist-deciduous forests. Oil in kernel varies from 57 to 80 per cent and is reputed to have very beneficial effect on growth of hair.

33. *Sterculia foetida* (*Punai*).

Occurs in Kolaba Division with 52.23 per cent oil in kernel.

34. *Tectona grandis* (Teak).

The whole seed contains about 1.57 per cent of oil. There are large plantations in the State and in Madras etc.

35. *Terminalia belerica* (Beheda).

The fruit is used in medicine and is a source of tanin also. (Beleric myrabolan). The oil in the kernels varies from 31.18 per cent to 45.33 per cent. The tree occurs scattered throughout India in deciduous forests.

36. *Thespesia populnea* (Bhendi or Tulip or Portia tree).

The species occurs in coastal tracts near Bombay. The seeds are observed to be rich in oil and deserve investigation.

37. *Vateria indica* (Indian Copal Tree).

Occurs in semi-evergreen and evergreen belt in Kanara. The seeds yield 50 per cent of a kind of tallow called "Piney Tallow" or "vegetable butter."

38. *Ventilago calyculata*.

It is a climber occurring in moist deciduous and evergreen forests. The kernels contain 60.4 per cent of oil.

In addition to the above list, the seeds of the species *Cinnamomum zeylanicum*, *Litsea* species, *Hopea odorata* and *Hopea wightianum*, *Machilus Macrantha*, *Sterculia urens* and some others which have not so far been investigated, require attention. Equally important are the oil yielding seeds obtainable from some herbs and shrubs occurring in forests, such as Mexican poppy, seeds of certain *Compositae*, *Enphorbiaceae*, *Solanaceae* etc.

Finally, it may be stated that on closer examination it may be found that there are many forests species of economic importance with dual or multi-purpose utility, that is to say, the seed may yield a valuable oil while the fruit parts or pericarp may yield edible products, like *Mohawa* flowers (corolla) and the tree may give timber etc. It is these species which require attention.

N. B. : The figures regarding percentages of oil in the kernels of seeds of various species listed above are quoted from work of Puran Singh as published in Indian Forester, No. 6., 1913.

GOKHRU (*XANTHIUM STRUMARIUM*) AS A SOURCE OF VEGETABLE OIL.

BY

R. C. SHRIVASTAVA,

Agricultural Chemist to Govt. of M. P., Nagpur.

Potentialities of "Gokhru" (*Xanthium strumarium*) as a source of vegetable oil, were recently reported by Shrivastava¹ *et al.* It was pointed out, that these plants, which grow abundantly through the hotter parts of India, have not found any use of economic importance and as such they are more a nuisance than a help. The study under reference brought out the fact, that an acre of land grow with these plants yield 500-600 lbs. of an oil bearing seed which contains 30-33 per cent oil. According to Bhatia and Joglekar² average yields of common cultivated oilseed in India such as til, linseed, mustard and castor range from 150-500 lbs. per acre. In comparison with this, the above yields of *Gokhru* is appreciable, and there appears to be a case for exploiting it as a source of vegetable oil.

The seed is enclosed in a thorny cover, which is hard and tenacious and is difficult to remove by mechanical means. A chemical treatment has, therefore been found for taking out the seeds. The treatment consists of soaking the thorny-fruit in 1.5-2.5 per cent sulphuric acid for about 12 hours and then drying in the sun. The fruit coat softens thereby and is easily crushed by light grinding. The seed is separated by winnowing in the usual way. The seed is usually of a dark olive colour and is soft enough for pressing without further treatment.

The oil obtained from the seed is of a pale yellow colour and is semi-drying in nature, having iodine value 112-24. Like certain other oils of this class, the Gokhru oil solidifies into a jelly on prolonged standing or by heating, and also dries slowly when exposed in the form of thin films. These properties suggest some uses in arts and surface coatings and they need further investigation.

2. Gokhru oilcake.

Another aspect of economic importance, is the value of the oilcake left after expressing the oil. The analytical data of the *Gokhru* oilcake along with those of others are given below :

Name of material (oil free)	Mois- ture	Minerals				N ₂ Substances		Fib- re.	Carbo- hydra- tes
		Total	SiO ₂	P ₂ O ₅	CaO	Nitro- gen Nx 6.25	Pro- tein		
1. Gokhru cake	7.93	7.06	0.16	3.29	0.22	9.67	60.44*	2.46	22.11
2. Groundnut cake	9.05	7.73	0.48	1.41	0.22	8.91	55.68	3.50	24.04
3. Til cake	6.69	11.11	3.43	2.30	0.44	6.78	42.37	5.77	34.06
4. Linseed cake	6.06	7.68	1.75	1.86	0.22	5.91	36.94	8.13	41.19
5. Almond seed	10.11	10.75	—	2.18	—	7.05	44.10	9.25	25.86
6. Soybean	5.98	6.00	0.094	1.30	0.25	7.36	46.04	7.68	34.30
7. Urid	7.39	3.57	—	0.89	—	3.95	24.69	5.98	58.37

* 25 p.c. of this is non-albuminoid.

From the above figures of analysis it is seen that *Gokhru* oilcake is remarkably high in its nitrogen content and in fact excels all the materials analysed for comparison. Its phosphoric acid content is also the highest. In view of these findings, *Gokhru* seeds from different sources were further analysed to see how far the high nitrogen and phosphoric acid contents were characteristic of the material.

	Nitrogen. (%)	Phosphoric Acid. (%)
1. Seed from 6' tall plants grown on land dumped with municipal wastes	9.70	3.46
2. Seed from 1' to 1½' tall plants grown on poor pasture land	9.50	3.08

From the results of analyses given above, it is seen that high amounts of nitrogen and phosphoric acid are a characteristic feature of the composition of *Gokhru* seed.

Phospholipid content of the *Gokhru* oil :

In view of the fact that *Gokhru* seed is rich in phosphoric acid the oil was also analysed for its P₂O₅ content. The oil was obtained by extracting the seed in a soxhlet apparatus with alcohol and ether.

The P_2O_5 per cent of the oil multiplied by 11.37, according to Elsdon³ gives the lecithin content of the oil. It was found to be 0.94 per cent. Maize oil according to the same authority contains over 1 per cent phospholipid and soybean oil according to Markley and Goss⁴ contains 1.5–2.5 per cent. The phospholipid content of the *Gokhru* oil is thus appreciable. There is, therefore, a possibility that exploitation of the *Gokhru* oil, may open up a new source for production and utilisation of lecithin in the country.

Manurial value of the cake :

Nitrogen and phosphoric acid are important manurial ingredients and they have a special value and interest in India, where soils are particularly deficient in respect of them. Manurial value of an oil-cake is judged by the nitrogen it contains and in this respect *Gokhru* oil cake stands quite high. The important consideration, however, is that the material should decompose readily in soils giving out nitrates, which are directly, utilised as plant nutrients. A nitrification experiment was, therefore, carried out to study the rate of decomposition of the *Gokhru* cake, the result of which are given below.

Rate of Nitrification of *Gokhru* cake in Black Cotton Soil.

No. of weeks		Nitrification (%)
2	...	72.79
4	...	74.20
5	...	79.46
6	...	76.05

Plymen and Bal⁵ in their study of the nitrifiability of different nitrogenous organic materials in typical soils of Madhya Pradesh found that, of the common oil-cakes usually, available for manurial purposes, the groundnut and linseed cakes nitrified most rapidly, namely 35 per cent at the end of two weeks. After this the groundnut cake gained over linseed and 77 per cent of it nitrified in 4 weeks. The maximum of 86 per cent nitrification was reached in 6 weeks time in the case of the groundnut cake. Castor cake nitrified slowly in the beginning, but reached its maximum of 72 per cent nitrification at the end of 6 weeks. Comparing these results with those of the *Gokhru* cake, the rate of nitrification and the total nitrification of *Gokhru* oil-cake are both sufficiently high. In fact, the amount of nitrification observed at the end of two weeks is very remarkable and appears to be due to the fact that, 25 per cent of the nitrogen is non-albuminoid, probably the amide form. The *Gokhru* cake has thus a very high manurial value and this fact should also to some extent, make the extraction of *Gokhru* oil an economical proposition.

References :

1. Shrivastava, R. C., Krishnamurty, R. S. & Athawale C. R.; *Journal of Sc. Ind. Res.* 1950, **9-B** No. 11, 282.
2. Bhatia, G. S. and Joglekar R. G.; *Nagpur Agri. College Mag.* 1950, XXIV Nos. 3 & 4, 1-6.
3. Elsdon, G. D.; *Edible Oils and Fats* 1926, 16.
4. Markley, K. S. and Goss W. H.; *Soybean Chem. & Tech.* 1944, 101.
5. Plymen, F. S. & Bal, D. V.; *Agric. Journal of India* 1922, XVII, 551-9.

DISCUSSION

Dr. J. S. Aggarwal (N. C. L.) enquired of Mr. Shrivastava, about the size of the *Gokhru* seed and whether oil had been obtained from it by pressure method.

In his reply, **Mr. Shrivastava** said that the seed was a little bigger than a wheat grain and slightly flattened, something like the seed of cucumber. As the commercial extraction had not been tried so far; he was unable to say anything more in that connection. However, he remarked, the seed was very soft, could be pressed with a finger and as such there should be no difficulty in getting the oil by expression.

KAMALA SEEDS (*MALLOTUS PHILIPPINENSIS*) AND ITS OIL.

BY

S. C. GUPTA,

National Chemical Laboratory, Poona.

Kamala seeds which contain 40–50 per cent of a fixed drying oil are obtained from a small evergreen tree called *Mallotus Philippinensis* belonging to the N. O. *Euphorbiaceae*. It is found throughout tropical India along the foot of the Himalayas from Kashmir eastwards to the height of 5000 feet all over Punjab, Uttar Pradesh, Assam, Bengal, Burma, Singapore and Andaman islands; and from Sind southwards to Bombay and Ceylon. It is also reported to be distributed in China, the Malaya islands and Australia.

The *Kamala* seeds are not being commercially exploited even upto today, yet the tree has been well known from early years because of the *Kamala* powder, which is collected from the exterior of the fruit. The powder has been in use as a dye and also a medicine. In India it was known even in 1535 A. D. as Kinbil, a sandy substance of red hue which was used as an anthelmintic and purgative. Atkinson reported that 2000 mds. of the powder was being exported from Kumaun (U.P.). The powder was first examined by late Prof. Anderson of Glasgow University who isolated a substance known as Rottelerin. Later on, the work on the constitution of Rottelerin was carried out by Brokman and Kaier, Narang and Ray and Robertson.

The seeds are black in colour and as mentioned by Kirtikar and Basu¹ when ground to paste, are applied to wounds and cuts. According to Watts² the seed oil is used medicinally in India. Many other writers have suggested that the oil is worth examining. The drying property of the oil was first mentioned by Brodie³ in 1937.

Some characteristics of the oil were reported by Singh and Saran⁴ in 1942 and later on in a note from the Forest Research Institute, Dehradun⁵. In their further work the Forest Research Institute in their annual Report (1948–49) reported the isolation of an acid melting at 77–78°C which they reported to be a mixture of an

isomer of licanic acid and eleostearic acid. They gave the constitution of the *Kamala* oil fatty acids as follows :—

Licanic acid isomer	...	27.6 per cent.
Eleostearic acid	...	31.0 „
Linoleic acid	...	2.6 „
Oleic acid	...	28.4 „
Stearic acid and other homologues of stearic acid		10.4 „
		100.0

The work on the constitution and utilization of this oil was started in the laboratories of C.S.I.R. in 1945.^{6,7} The fresh and sound seeds yield about 40 per cent oil of their weight of pale white kernels. The colour of the kernels become yellow and then brown as the seeds become old and at the same time, the amount of the oil in them also goes on decreasing. When ether is used as the solvent, a yellowish translucent extract is obtained which is probably due to the presence of a semi-polymerised resinous material extracted from the seeds along with the oil. A clear extract is, however, obtained when benzene is used as solvent. The distillation of the solution to remove the solvent, however, requires heating for a relatively long time and the oil sets to a gel after a few days. Light boiling petrol ether has been found to be the most suitable solvent for the extraction of the oil.

Some of the characteristics of the oil obtained as above (1) and the results given by Singh and Saran (2) and F.R.I. (3) are as follows :—

	1	2	3
Acid value	6.4	11.3	19.04
Saponification value	195.0	207.6	170.3
Acetyl value	15.7	46.8	49.24
Henner value	95.6	96.1	—
Hexabromide value	0.3	—	—
I.V. (Wijs)	166.8	157.3	180.3 (Hanus)
I.V. (Wobern B)	175.8	—	—
Diene value (Ellis & Jones)	40.4	—	—
Carbonyl value	Nil	—	—
Brown's heat test	9'-30"	—	2'-30"

It may be remarked here that Brown's heat test of F.R.I. is very low but it may be pointed out that the value obtained even by us is less than that of Tung oil.

The total saturated acids by Bertram oxidation method has been found to be 12.3 per cent, I.V. 0.3 and neutralization value 227.3.

The separation of the total *Kamala* seed oil fatty acid into saturated and unsaturated constituents by usual lead salt alcohol method has not been found possible. The results are as follows :—

	I.V.
Lead salt alcohol soluble fatty acids	177
„ „ „ insoluble „ „	143
A part of the acids polymerised during this treatment.	

By employing the procedure of Kaufmann and Baltes for the removal of eleostearic acid from Tung oil fatty acids as given below, an unsaturated fatty acid melting at 86–87°C has been obtained. Petrol ether was added to the total fatty acids and the mixture was irradiated in the presence of traces of iodine by ultraviolet light. The fatty acids which separated out were crystallized from benzene; m.p. 86–87°C. Neutralization equivalent 293.3, Diene value 120.7, iodine value (Wobern B) 249.6. The acid is soluble in alcohol, ether and carbon tetrachloride but insoluble in petrol ether. It is unstable and polymerises to a rubbery mass in two days. The acid was hydrogenated in the presence of platinum catalyst and was found to absorb hydrogen equivalent to three double bonds. The reduced acid which is quite stable crystallizes from ethyl acetate and benzene; melting point 98–99°C, C–71.41, H–11.69 per cent. Empirical formula $C_6H_{12}O$ equivalent weight by silver salt method–309, titration method–304.5; mol. wt. by Rast's camphor method 334. The reduced acid thus can be given the formula $C_{18}H_{36}O_3$ corresponding to the molecular weight 300.

It was later on found that by shaking the total fatty acids of the oil with cold petrol ether, an acid separates out, which crystallizes from benzene and acetone, m. p. 77–78°C, Neutralization equivalent 293.12; I. V. (Wijs) 185, I. V. (Wobern B) 248.6, Diene value (Ellis and Jones), I. V. 120.61; (Wijs 2 mts.) 173–6; Diene value by difference of I. V. total and 2 minutes Wijs, 75. It absorbs bromine equivalent to about two double bonds.

The acid on suspension in petrol ether in a quartz flask in the presence of traces of iodine, on irradiation with ultraviolet light, gives an acid melting at 87–88°C which corresponds to the one mentioned earlier. It was further found out that on reduction, an acid melting

at 98–99°C was obtained which is also the same as stated above. The two acids have been provisionally named as α - and β -Kamlolenic acids. Their carbon and hydrogen analyses are as follows:--

	C%	H%
α -Kamlolenic acid	73.2	10.27
β -Kamlolenic acid	72.7	9.97

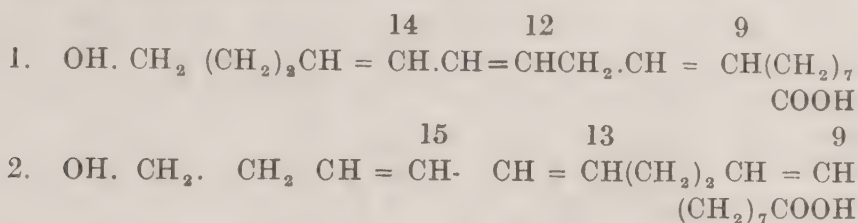
On calculation, the empirical formula is $C_6H_{10}O$. Since the reduced acid has the mol. wt. 300, and corresponds to the formula $C_{18}H_{36}O_3$ the α - and β -Kamlolenic acids can be given molecular formula $C_{18}H_{30}O_3$.

It may be remarked here that the Diene value as determined by Ellis and Jones method is much more than that of eleostearic acid, where all the three double bonds are in the conjugated position. The fact that the reduced acid has the mol. wt. 300 and contains 3 oxygen atoms leads to the conclusion that the third oxygen atom in the reduced acid as well as in α - and β -Kamlolenic acids is present either in the form of carbonyl group or hydroxyl group. Because the original oil has no carbonyl value and moreover α - and β -Kamlolenic acids do not give any phenylhydrazone or semicarbazone, the keto group might be absent in both the acids. The reduced acid gives an acetyl derivative melting at 72°C, and acetyl value 164. So the reduced acid has a hydroxyl group. Its presence and position is further proved by its oxidation to a C_{18} dibasic acid melting at 124–125°C. This acid has been confirmed as hexadecamethylene 1:16-dicarboxylic acid ($C_{18}H_{34}O_4$). The fact that a dicarboxylic acid of same number of carbon atoms is obtained from the oxidation of the reduced acid shows that a hydroxyl group is present in the terminal position. The reduced acid has, therefore, proved to be the well known ω -hydroxy stearic acid.

From the above it will be quite safe to assume that the hydroxyl group must be present in the unsaturated α - and β -Kamlolenic acids in terminal positions also. This explains the high diene value by Ellis and Jones method. Maleic anhydride is known to react with hydroxyl group to some extent.

The positions of the three double bonds in the α - and β -Kamlolenic acids have been established by their permanganate oxidation products and those of their maleic anhydride adducts. These investigations lead to the conclusion that at least two double bonds are present in the conjugated positions, and the two acids may be

represented by any one of the following formulae, the isomerism is most probably geometrical about one or more of the double bonds.



Further elucidation of the position of the double bonds in these two isomers will be known from the study of their ultra-violet and infra-red absorption spectra which is now under progress. The other acids in total *Kamala* oil fatty acids are also being investigated.

Work on the possible utilization of these important compounds is also underway at the National Chemical Laboratory, Poona and a patent on these compounds has already been obtained in India and U. K.

Kamala seed oil has been found to be even superior to tung oil in various coating compositions. The utilization of the oil in the preparation of air drying wrinkle finish varnishes and paints has been a subject of patent both in India and U. K. Further work on these lines is in progress.

KAMALA SEED CAKE

The seed cake after removal of the petrol ether and ether sulphuric soluble fractions was found to have the following constituents:

Moisture	2.86 per cent
Ash	6.98 „
Crude fiber	6.57 „
Proteins	48.12 „
Carbohydrates	35.47 „

The sufficiently high amount of proteins give an indication that the seed cake can be used in the formation of adhesives and plastics and also will be a useful fertilizer.

References.

1. Kirtikar and Basu; Indian Medicinal Plants 1918, Part II, pp. 1165.
2. Watts, G., Dictionary of Economics Products of India 1891, 5, pp. 122.

3. Brodie, N.; Bull. Indian Industrial Research No. 10, 1937. pp. 33.
4. Singh, B. K. and Saran, B.; *Current Science*; 1942, 11, 360.
5. Forest research in India and Burma 1941-42. Part I, pp. 42.
6. Aggarwal, J. S., Bhatnagar, S. S.; Narain, Prakash and Karimullah; *J. S. I. R.*; 1948, 7B, 136-138.
7. Gupta, S. C.; Sharma, V. N. and Aggarwal, J. S.; *J.S.I.R.*; 1951, 10B, 76.

DISCUSSION :

Mr. Om Prakash Oil Expert to U. P. Govt. referred to the work carried out at the H. B. T. I. Kanpur on *Kamala* seed oil wherein the results obtained agreed more to those of the N. C. L. than those of Forest Research Institute Dehra Dun especially the Sap. value and Brown's heat test. Extraction of the oil by pressure method was not found quite suitable, which might be due to high melting point of the fat (Ca. 60°C). He even experienced difficulty in the solvent extraction of the oil as it used to polymerise while removing the solvent which had to be distilled under vacuum. He, therefore, suggested that some better method should be found for extracting this oil.

Dr. J. S. Aggarwal (N. C. L.) agreed with Mr. Om Prakash that pressure method of extraction of the oil was not found suitable due to the high viscosity of the oil and its rapid polymerisation even at 80-100°C required for easy flow of the oil. As regard solvent extracted oil, varied consistencies and colours were obtained depending upon the solvents used for extraction just like Tung Oil. He further informed that if 5 per cent of petrol ether be allowed to remain in the oil, it could be kept for a sufficiently long time without changing into a gel.

Mr. S. C. Gupta informed that the Forest Research Institute Dehra Dun claimed to have evolved a process of extracting *Kamala* oil by which the oil could be kept for a sufficiently long time without polymerisation.

Mr. N. S. Bharatia of the Elephant oil mills, Bombay wanted to know about the keeping qualities of *Kamala* oil paints and varnishes without petroleum ether, because it might not be possible to use the latter solvent due to its low flash point. Moreover, whether alkyls

and water and alkali resistance varnishes could be obtained from the oil and if experiments of the reactivity of this oil with basic substances like zinc oxide were carried out.

Dr. Aggarwal informed that they had prepared air drying wrinkle finish varnishes from *Kamala* oil. The varnishes could give wrinkles alright even after a year and so the materials stood the time alright. Such a paint was applied on the masonite sheets fixed at the doors of the lifts of the N. C. L. a year back. They were also water and alkali resistant. Work on the preparation of other types of coating compositions from the oil was in progress.

UTILIZATION OF NIM OIL (*MELIA INDICA*)

BY

CHITTARANJAN MITRA

National Chemical Laboratory, Poona.

Introduction: Nim and its uses:

Nim or Nimba (*Melia indica*; *Melia azadirachta*: *Azadirachta indica*) which belongs to the Natural Order, *Meliaceae*, is indigenous to this sub-continent and is cultivated throughout the country on account of the medicinal properties attributed to it since ancient times. Its twigs are used as tooth brush for general mouth hygiene. Decoctions of the leaves and bark are used as a febrifuge while the bark is also employed for healing unhealthy wounds and ulcers and in the treatment of a variety of skin troubles, jaundice, prurigo and liver complaints. The fruits are reputed to act as a purgative, emollient and anthelmintic, and are also used in the treatment of urinary troubles, piles etc.

The nim oil commonly known also as 'margosa oil' which constitutes nearly 45 per cent of the seed, is largely used by the villagers as hair tonic, and is particularly reputed as a cure for rheumatism, scrofulous glands, leprosy and a variety of skin affections. An interesting use of the oil was recorded by Buchanon Hamilton who stated that in South India, about an ounce of the oil was being administered orally to woman immediately after she was delivered of a child. The various parts of the plant with age-old reputation for their medicinal properties have been in much use even by the practitioners of Western system of medicine¹⁻⁵.

Earlier work:

The medicinal properties of nim have been rightly attributed to the bitter constituents which are mostly concentrated in the seed kernel, and attempts have, therefore, been made by various research workers to isolate the active constituents from the nim oil. Investigations on this problem have, however, led to findings of a very conflicting character, without yielding any well-defined products which could, either be employed in pharmaceutical practice, or made the subject of further chemotherapeutic studies. Thus the so-called 'margosic acid' claimed by Roy and Chatterjee⁶ as a new acid was

subsequently shown by Dutt and Roy⁷ to be just a mixture of well known fatty acids with some bitter resinous impurities. Watson *et al*⁸ isolated 'margosopicrin' in a yield of 0.012 to 0.017 per cent from the soap lyes of the oil and an amorphous bitter acid in an average yield of 0.15 to 0.24 per cent. Sen and Banerjee⁹ noted the isolation of a sulphur containing acidic bitter (yield not mentioned) from the aqueous extract of the oil. Qudrat-i-Khuda¹⁰ and co-workers communicated the isolation of a water soluble bitter from the aqueous extract of the oil after subjecting it for long periods to steam distillation. Four new fatty acids claimed to have been isolated by them, were later on found to be mixtures of common fatty acids by Child and Nathanael¹¹. Seshadri *et al*¹² reported the isolation of the two 'dark brown' and 'grey' amorphous bitters (yields not given). The process of isolation adopted by Seshadri *et al* was based on the hot continuous extraction of the oil with methylated spirit for 30 hours.

Present investigations:

In so far as the methods employed by the earlier workers appeared to be of too drastic a character to ensure the isolation of the bitter constituents in the form in which they can be presumed to occur in the plant body, and in view of the growing importance of nim, the *Council of Scientific and Industrial Research* at the initiative of Dr. S. Siddiqui, undertook a scheme of systematic investigation into the bitter constituents and eventual utilization of the nim oil (the utilization of the nim seed based on the researches carried out under the C.S.I.R. is schematically shown in the accompanying chart), when a series of new crystalline and amorphous bitter constituents, provisionally named as nimbin, nimbinin, nimbidin, and a liquid oil soluble bitter fraction, nimbidol, were isolated from the oil in total yield of about 2 per cent on the weight of the oil, by a process of separation with the help of solvents, mainly alcohol, under the mildest possible conditions ensuring isolation of them in the form in which they can be presumed to occur in the plant body. Working on the commercial samples of the oil as well as raw materials obtained from various sources and collected under personal supervision, definite standards for the yields and purity of the various bitters have been fixed and a number of pharmaceutical products with nimbidin, the main active bitter principle, and its derivatives, have been prepared¹⁶⁻²¹.

Nimbidin, the major active bitter constituent, obtained in an yield of about 1 to 1.5% on the weight of the oil, is a straw-coloured, water insoluble, oil or petrol-ether insoluble, granular powder of

neutral character. It is an ester of terpenic origin as the other bitter constituents of this series. It is bitter in aqueous emulsions even in dilutions of over 1 in 100,000 with the taste of fresh nim twigs. It is soluble in alcohol, methanol, acetone, ether, ethyl acetate, benzene, chloroform and insoluble in dilute acids and alkalies, and gives no colour reaction with ferric chloride.

Nimibdin is dextrorotatory ($+65^\circ$) and its analysis gave C, 68.5 per cent; H, 7.8 per cent. Apart from yielding a small fraction of residual nimbin crystallisate, when nimbidin is treated with caustic alkalies under controlled conditions of temperature, concentration of alkali and duration of the reaction, it yields a neutral amorphous product of ketonic character and subsequently a crystalline neutral product, neonimbidin (222°C), a crystalline acid, nimbidic acid (235°C) and an amorphous bitter acid, nimbidinic acid, constituting the main product of hydrolysis. Salts of nimbidinic acid are more stable and physiologically more active than nimbidin itself. By adjusting the experimental conditions, it is possible, either to get all the products referred to above by a process of fractional hydrolysis, or to obtain amorphous nimbidinic acid on a single operation. In this connection, however, it is to be noted that on treatment with higher concentrations of caustic alkalies which are often employed for the saponification of oils, nimbidin and allied bitter constituents are destroyed to soluble and insoluble resinous products, and which simultaneously render the resultant soap bitter and foul smelling, and thus, neither the bitter constituents of therapeutic values can be isolated from the oil nor a soap of good quality can be obtained from it. Nimbidinic acid appears to contain some organically combined sulphur which as in the case of nimbidin, cannot be removed by any process of separation with the aid of solvents.

Nimbin, the major crystalline bitter, $\text{C}_{28}\text{H}_{40}\text{O}_8$, m. p. 205°C (yield 0.12 to 0.18 per cent) is a sulphur-free, neutral, water insoluble, highly dextrorotatory ($+170^\circ$), colourless crystalline product having similar solubilities as of nimbidin. It also gives no colour reaction with ferric chloride. On alkaline hydrolysis, it first yields a ketone, m. p. 250°C and subsequently two crystalline acids melting at 263°C and 161°C respectively. On acid hydrolysis it gives a crystalline neutral product melting at 218°C . Similar to nimbidin, on distillation with zinc dust, nimbin yields a steam volatile terpenic oil having the molecular formula $\text{C}_{15}\text{H}_{22}\text{O}_2$.

Nimbinin, m. p. 192°C (yield 0.01 per cent), is of similar characteristics as those of nimbin.

Nimbidol, the liquid bitter fraction on further investigations appeared to be a mixture of nimbidin or its degradation products together with some glycerides, as on hydrolytic degradation, it also yielded the same crystalline and amorphous products obtained from nimbidin as well as a liquid bitter acid which on further fractionation after esterification yielded non-bitter fatty acids. The nimbidol fraction also contains the comparatively greater proportion of the sulphur containing odorous constituent of the nim oil which has been separated as a volatile oil by alcohol-vapour and steam distillation of the bitter fraction.

Chemical examination of the various parts of nim and bakayan :

As a result of systematic investigations, it has since been established that the nimbidin series of bitter active constituents are distributed and present in the native state in the plant body in as much as the amorphous bitter nimbidin as well as the crystalline bitters, nimbin and nimbinin have been isolated from the alcoholic extractive of the trunk²² and root bark²³⁻³⁶ of the plant. The leaves²⁴ yielded two amorphous bitter acidic constituents apart from the carotenoids and other subsidiary products. The blossoms²⁵⁻²⁷ yielded a characteristic essential oil (yield 0.5 per cent), a flavone²⁸ which has since been identified as kaempferol, the sterol and its glycoside, a saturated hydrocarbon, nonacosane $C_{29}H_{60}$, mp. 64–66°C; but no bitter principle has been found to be present in the blossoms as well as in the exudate²⁹ of the plant. It may be mentioned here that Bakayan (*Melia azadirach* Linn), a sister plant of nim, belonging to the same Natural Order, yields an amorphous bitter, bakayanin³⁰, similar to Nimbidin, from its fruits and bark. It is interesting to note that in the case of bakayan, unlike nim, the seat of the bitter constituent is the fruit pericarp and the fixed oil from the kernel is absolutely free from the bitter principles. The sterol which has been found to be present in all the parts of the nim tree is also present in bakayan. The sterol-glycoside obtained from the nim blossoms, has also been isolated from the bakayan bark (unpublished work).

Pharmacology and therapeutic evaluation:

Nimbidin has very little toxicity, the lethal dose tried on frogs, being 25 mgm. per gm. body weight. Both nimbidin and sodium nimbidinate, a water soluble salt of nimbidinic acid, have no bactericidal or bacteriostatic action *in vitro*. The preliminary pharmacological investigations indicate that both nimbidin and sodium nimbidinate stimulate uterine contractions, the latter having a very powerful action

on the virgin uterus of guinea pig even in dilutions of 1/25,000, while nimbidin acted upto 1/2000 dilution. Both the drugs have been found to have action on *Paramecium caudatum*. Emulsions, liniments and ointments of nimbidin in strength of 1/2000, 1/100 and 1/100 respectively, when used externally, showed very promising results in cases of skin affections like scabbies, dermatitis, farunculosis, herpes labialis and ulcers due to burns.

Now, that the bitter constituents of nim have been isolated in industrially workable yields and preliminary pharmacological studies and therapeutic trials with the main active bitter principle, nimbidin and its derivatives indicate promising results, it is expected that the medicinal importance of the plant will be established on a more scientific basis and the therapeutic application of the bitters will be developed with speed. While the studies in the chemistry of the various products isolated from nim are being actively pursued in the National Chemical Laboratory, a close collaboration with the Central Drug Research Institute is being effected for the development of the pharmacological studies and therapeutic aspects of these active principles. Effective co-ordination of chemotherapeutic studies in the bitters with the outcome of pharmacological investigations in them would, it is hoped, soon result in the development of some specific uses of these active constituents. The physiologically active bitter principles isolated from the nim oil will, not only, constitute an important by-product in the scheme of industrial utilization of this oil, but it may be emphasised here, that the separation of these bitter principles is an essential prerequisite to obtain the fixed oil of the nim seeds in a pure and refined condition so that economic exploitation of this important raw material in industry is assured.

Industrial utilization of 'extracted' nim oil:

Solvent extraction of the bitter constituents of the nim oil leaves the oil in a purified state for industrial purposes such as manufacture of soaps, medicinal cosmetics, disinfectants, emulsifying compositions for insecticidal sprays etc. During the course of further investigations with the oil left after extraction of the bitter constituents, it has been possible to prepare technical 'stearin' and 'oleic acid' of good quality in substantial yields by a comparatively easier method of separation of the solid acids from the liquid ones by fractional crystallisation. The conditions of pyrolytic degradation of the 'extracted' oil have been studied and the products of degradation are being investigated with a view to their probable industrial uses. The residual odorous sulphur containing compound responsible for

the foul odour of the oil, left in the 'extracted' oil, has since been removed, and finally it has been possible to obtain the oil as a colourless, non-bitter product without having any foul smell. The refined oil thus obtained can be easily hydrogenated.

Fixed oil of nim seed—not a medicinal oil: Its component fatty acids :

The fatty acids of the nim oil and its glyceride composition have been a subject of critical study by a number of workers since 1917⁶⁻¹¹,^{13 15}. Mixtures of fatty acids contaminated with hydrolytic degradation products of the bitter constituents, depending upon the treatment of the oil, had been claimed to be the active principles of the nim oil, thus attributing medicinal value to the oil (glycerides) itself. Newer fatty acids had also been claimed to have been isolated. In the course of the later investigations the above findings have since been disproved from time to time. Here, the following remarks by Hilditch and Mutri¹⁵ while recording the results of analysis of the fatty acids and glycerides of nim oil in 1939, are worth recalling— " the presence of characteristic non-fatty compounds which confer on nim oil certain medicinal properties and an unpleasant odour, led to difficulties in one stage of the analysis and to consequent less certainty than usual in some of the numerical results"— and "these non-fatty substances possess an unpleasant odour and include organic compounds of sulphur; saponification of the fat with alkali is accompanied by the liberation of hydrogen sulphide. These properties, of course, make nim oil unsuitable for use in edible fats, or in the absence of drastic refining (e. g. distillation) of the fatty acids, for soap of good quality".

Now, when the bitter constituents have been separated from the oil as different chemical entities, and the oil has been freed of the foul smelling odorous principle and further refined rendering its hydrogenation possible and easy, it can be safely stated that the medicinal properties of the oil which are due to the bitter active principles have got no relation with the fixed oil of the nim seed. Moreover, these bitter principles have since been found to be distributed in other parts of the plant as they have been isolated from both root and trunk bark (*loc. cit.*). Thus it is evident that the fixed oil of the nim seed does not possess any medicinal properties as is the case with the chaulmoogra (*Hydnocarpus kurzii*) oil or the gorli seed (*Oncoba echinata*) oil having C_{16} and C_{18} constituent acids containing cyclopentenyl ring, or the castor oil having the constituent ricinoleic acid. The nim oil which has now been obtained in a

refined state, is a non-drying oil having no polyethenoid acid in it. It is a sufficiently stable oil and does not develop free acidity on keeping. The oil is rich in oleic and palmitic acids and contains comparatively a good amount of stearic acid. Analysis of the refined oil, carried out by employing the recently developed method of low temperature crystallization and ultraviolet absorption spectroscopy, shows the following fatty acid composition of the oil : myristic 2.4%, stearic 10.2%, palmitic 16.8%, arachidic, 1.7%, oleic, 59.9%, and linoleic 8.3%; unsaponifiable matter being 0.7%.

Like other vegetable oils, nim oil freed of the bitter constituents can be, of course, used for the manufacture of soaps, but in consideration of its special characteristics and the fatty acid composition, the 'extracted' nim oil may be particularly put to other industrial uses such as production of technical oleic acid and 'stearin', the pyrolytic degradation products of the oil, or high melting stearin after hydrogenation.

Nim oil as a rich source of technical oleic acid and 'stearin' :

This oil which has not been hitherto] exploited is a very rich source of 'oleic acid' and 'stearin' which have been obtained in yields of 63 and 26 per cent respectively on the weight of the 'extracted' oil. The 'stearin' obtained from the 'extracted' nim oil melts at 58-61°C, and the technical 'oleic acid' referred to, has an iodine value of 86.

Pyrolytic degradation products of 'extracted' nim oil :

Before refining and removal of the odorous principles the oil left after extraction of the bitter constituents, when subjected to pyrolytic degradation, yield 90-93% of distillate without any cracking agents, below the distilling temperature 300°C (comparing the much higher distillation range for the cracked products from the common vegetable oils^{3,4}). The splitting up of the glycerides and the comparatively easier pyrolytic degradation of the fatty acids of the 'extracted' nim oil is presumably due to the presence of the terpenic sulphur containing compound. On further fractionation of the total distillate of the 'extracted' oil, the following fractions (Table I) were obtained and characterised.

TABLE I

Fractions	Boiling range °C	Yield (appx)%	Sap. Value	Acid value	Refractive index at 29.5°C
I	40-80	8	40.3	8.0	1.4157
II	90-120	15	78.8	46.9	1.4271
III	130-160	12	66.9	48.8	1.4345
IV	180-200	22	90.8	74.9	1.4451
V	220-260	18	58.6	44.2	1.4577
VI	260-290	15	negligible.	...	1.4824
Extracted nim oil		...	198	...	

From a comparative study of the different fractions of the distillates by using a cracking agent, zinc chloride or without it, there seems to be no particular advantage to use a cracking agent in the case of this oil. The following fractions (Table II) were obtained by distilling the 'extracted' nim oil with 1% zinc chloride.

TABLE II

Fraction	Boiling range. °C	Yield %	Sap. Value	Ref. Index. at 28°C
*I	below 200	10	100.4	1.4285
II	200-250	30	110.9	1.4423
III	250-290	35	48.3	1.4594

* Fraction I yielded a crystalline product (10% yield) melting at 65-72°C, ultimate analysis of which showed it to be a saturated hydrocarbon.

The pyrolytic degradation products of the 'extracted' nim oil may be used as solvent, illuminant, thinner for the paints and varnishes and for insecticidal sprays.

Deodorization of the 'extracted' nim oil and its further refining :

The oil left after extraction of the bitter constituents still retained a part of the odoriferous constituent, a sulphur containing compound of terpenic nature, responsible for the foul smell of the oil. While the oil left after the extraction of the bitter is sufficiently good for the purpose of manufacture of soap, technical 'oleic acid' and 'stearin' as well as for the pyrolytic degradation products or for a

number of other uses, but to ensure better industrial utilization of the oil, it was of considerable importance to obtain the oil free from the odorous principles and to further refine it subsequently. Although usual steam distillation of the 'extracted' nim oil very slowly removes the difficultly volatile sulphur containing odoriferous constituents, but prolonged steam distillation particularly at comparatively higher temperatures decomposes them enhancing the foul odour of the oil, apart from splitting the glycerides to a considerable extent and thus adding to the free acidity of the oil. By processes ³⁵ evolved in this Laboratory for the deodorization and subsequent refining of this oil, it has since been possible to obtain the 'extracted' nim oil as a colourless product having no undesirable taste or smell, and which can be easily hydrogenated. The saponification equivalent of the refined nim oil is 290; its acid value 0.5; and iodine value 68.

Hydrogenation of 'refined' nim oil and the resultant products :

During the process of hydrogenation of the refined oil in Parr's medium pressure hydrogenation apparatus using the industrial nickel catalyst, the following samples (Table III) of partially hydrogenated and final products were taken and their iodine values determined :

TABLE III.

Products	Consistency.	Iodine value.
Refined oil	liquid	68
Hydrogenated :		
Sample I	Partly solidified	65
Sample II	Soft solid m. p. 35-40°C	52.7
Sample III	Brittle solid m. p. 50-54°C	3.2

The hydrogenated nim oil (iodine value 3.2) on saponification yielded crude 'stearin' melting at 60-64°C which on crystallisation from alcohol yielded shining flakes melting at 64-65°C.

The refined nim oil or its hydrogenated products when put to industrial production will, not only, substantially ease the present acute position of the fats and oils but will release the enormous quantities of edible oils which are now being added to the soap stock. The 'stearin' from the hydrogenated nim oil may be of use to the cosmetic industry as well as for textiles, leather and rubber processings, apart from the manufacture of candles.

Collection and processing of nim seeds and production of the oil :

In the course of these investigations it was, however, observed that the crystalline bitter principles, nimbin and nimbinin, could not be obtained from certain samples of solvent extracted oil, and that their yields from oils from various sources varied within an appreciable range. When it has since been established that these bitters along with nimbidin occur as such in the plant body and are distributed in the root and trunk bark of the plant as well, the apparent absence of the crystalline bitters in certain samples of oil may be considered as due to variations in the state of maturity of fruits at the time of their collection. Variations in the yields of the bitters, which are of terpenic origin and are labile esters undergoing, even under mild conditions, changes particularly of hydrolytic nature, are largely dependent on the quality and age of the oil and thus evidently on the maturity of the seeds, their processing, drying and storage conditions. Apart from the above findings, the difficulties in collection, processing and storage have since been taken into consideration by the Indian Central Oilseeds Committee. A few observations from the Committee's Report^{3 1} of December, 1950 are noted below :

“ Nim seed crop comes in rainy season and unless the seed is dried before being stored, its high moisture content leads to heating and subsequent charring of the seeds during storage. Due to want of proper methods and equipment for drying nim seeds, most of this important seed in the country is wasted”.

It may be suggested here that the ripe nim seeds should be depulped without resorting to washing, and the seeds should be dried in shade as quickly as possible. After decortication the kernel may be stored in cool dry place. The kernels are soft enough to ensure good yield of oil by cold pressing and continuous hot solvent extraction should not be encouraged in view of the labile nature of the bitter constituents.

“ The main difficulties at present in harnessing of such a plentiful resource of oil are”, according to the Report, “(i) the harvest of the nim fruit is obtained within a very short time in the beginning of the rainy season, (ii) the seed obtained contains lot of moisture and deteriorates quickly during storage, (iii) the oil possesses an unpleasant odour. The seed while in storage often gets so much charred on account of the heat produced by auto-oxidation during storage that no oil can be pressed out of it. In order to encourage the development of nim seed crushing industry, the following investigations are necessary : (i) to find out proper method of treatment of nim fruit to produce good dry nim seeds which can be stored throughout

the year, (ii) to work out best method of crushing the seed, and (iii) to treat the nim oil produced so as to remove its unpleasant odour”.

The report adds, “It would also be necessary to make a survey of the present and prospective availability of the nim seed in the country for which no figures are available so far ...” Again, according to the Committee, “So long as there is no sustained effort to collect nim seed, the survey will serve no purpose. Moreover, the tree grows wild more or less throughout the country. All that is possible will be to get rough and ready estimates from the States where the tree grows in great abundance. Once the industrial possibilities of nim oil are established and a demand is created, the collection and utilization of the seed will automatically follow”.

In its latest report and in a very recent memo³² the Indian Central Oil seeds Committee is reported to have carefully considered the processes developed in the C. S. I. R. laboratories for separation of the bitter constituents from the oil and its simultaneous purification and recommended the commercial possibilities of the work to be explored.

Absence of organised collection of nim seed and the present limited use of the oil :

As is evident from the fact that there is no organised collection of the seeds and no authentic data on the production of the oil, which is only sporadically carried out here and there by villagers, this oil is not yet a trade commodity as there seems to be no regular demand for it. Apart from its very limited use for illumination purposes in the rural areas, whatever quantity of the oil is available in the cities, is only to feed the scanty requirements of the practitioners of the indigenous systems of medicine. Under the circumstances there is no possibility of this oil being adulterated at the moment and upto now, no report is seemed to have been appeared in regard to adulteration of this oil. Moreover, no other vegetable oil is cheaper than the nim oil, or no other oil bearing seed having such considerable yield, is going such a huge waste.

Although no reliable data are available in regard to production of the nim seeds, but according to the Indian Central Oilseeds Committee, in U.P. alone, the number of (avenue) trees in Municipalities and on the State and district roads only, is estimated to be over 3 millions which would yield about 4.5 million maunds of seeds annually. The report states,—“most of the nim fruit is, however, not collected but allowed to go waste. At some places, some of the fruits are collected and treated to produce the seed from which the oil is obtained by pressing either in *ghanies* or in handscrew presses. But the

collection and pressing of the seed is not yet practised on any scale commensurate with the huge quantities of fruits produced."

From the availability and production figure of *nim* oil collected from the southern Indian States, it seems that in Madras and Mysore, a small quantity of the oil is produced which is used mostly for illumination, medicinal uses and partly for production of soaps. In this connection, it may be stated, that the quality of the *nim* seed and its oil content seems to be poorer in South India than that from the trees grown in the North where they are also in much larger number.

In regard to the manufacture of soap from *nim* oil, it may be stressed that, as has already been pointed out, the active bitter constituents of the oil are totally destroyed by any drastic chemical treatment and as such the usual methods of soap manufacture with this oil can neither, certainly, ensure the medicinal properties of the oil to be present in such soaps, nor a good quality soap can be obtained.

Alcohol extraction of *nim* oil and proper industrial utilization of the oil and its active bitter constituents:

To effect proper industrial utilization of the *nim* seeds, it is imperative that the oil is first treated with solvent (alcohol) to extract and separate the bitter constituents, and then subject it to subsequent deodorization and refining when not only the bitter constituents are obtained as a valuable by-product but the oil is also obtained in refined condition suitable for various industrial uses as discussed in the preceding pages. Rectified spirit, the solvent employed for this purpose, apart from the working loss, most of which can be recovered and re-used, is not only the cheapest but can be produced in any quantity in this country, and its artificial non-availability at a reasonable price, should not, perhaps, be allowed to prejudice the effective industrial utilization of such an important raw material which has hitherto been a colossal waste.

Now, that the Indian Planning Commission³³ has finalised a programme for the production of *nim* oil as a part of the scheme for the development of cottage industries, entailing a cost of more than one million rupees per year, and when the Indian Central Oilseeds Committee is actively considering the scheme of organised collection and processing of the *nim* seeds, it is hoped that the processes developed by the long range programme of research under the Council of Scientific and Industrial Research will be fully exploited for the industrial utilization of *nim* oil on scientific and economic basis.

Acknowledgment.

The author's grateful thanks are due to Dr. S. Siddiqui for initiating this scheme of research, and for his valuable

contribution and guidance. "Thanks" are due to Mr. S. Bhattacharji, Mr. P. Narsimha Rao, Mr. S. N. Ghatak and Dr. S. S. Gupta for their collaboration from time to time. Thanks are also due to Dr. R. C. Shah and Prof. J. W. McBain for their keen interest in the present investigations.

References.

1. Dymock, *Pharmacographica Indica*, 1890, **1**, 324.
2. Watt, *Dictionary of Econ. Products of India*. Vol. V. 215.
3. Dutt, *Materia Medica of the Hindus*, 1922, p. 139.
4. Fischl and Schlossberger, *Chemotherapy* (Eng. Edn.), 1933, p. 321.
5. Chopra, *Indian Medicinal Plants*, 1932, p. 343.
6. Roy and Chatterjee, *Ind. J. Med. Res.*, 1917, **5**, 656.
7. Dutt and Roy, *J. Soc. Chem. Ind.*, 1929, **48**, 333T.
8. Watson *et al*, *ibid.* 1923, **42**, 387T.
9. Sen and Banerjee, *J. Ind. Chem. Soc.*, 1932, **8**, 773.
10. Qudrat-i-Khuda *et al*, *ibid*, 1940, **17**, 189.
11. Child and Nathanael, *J. Ind. Chem. Soc.*, (Ind. Edn,) 1944, **21**, 35.
12. Seshadri *et al*, *Ind J. Pharm*, 1940, **2**, 201.
13. Child and Ramanathan, *J. Soc. Chem. Ind.* 1936, **55**, 124 T.
14. Dasa Rao and Seshadri, *Proc. Ind. Acad. Sci.*, 1942, **15**, 16.
15. Hilditch and Murti, *J. Soc. Chem. Ind.*, 1939, **58**, 310T.
16. Siddiqui, *Curr. Sci.*, 1942, **11**, 278.
17. Siddiqui & Mitra, *J. Sci. Ind. Res.*, 1945, **4**, 5.
18. CSIR, Non-Tech. Note No. 32., *J. Sci. Ind. Res.*, 1946, **5**.
19. Siddiqui and Mitra, *Ind. Pat. No.* 33649.
20. Siddiqui and Mitra, *Ind. Pat. No.* 33650.
21. Siddiqui and Mitra, *Ind. Pat. No.* 36651.
22. Bhattacharji, Mitra and Siddiqui, *J. Sci. Ind. Res.*, 1949, **VIIIB**, 187.
23. Mitra, Rao and Siddiqui, *Proc. Ind. Sci. Cong.*, Pt. III, Abs. 1947.
24. Mitra and Siddiqui, *Proc. Ind. Sci. Cong.* Pt. III, Abs., 1948.
25. Mitra, Rao, Battacharji, Siddiqui, *J. Sci. Ind. Res.*, 1947, **6B**, 19.
26. Subbaramanian and Rangaswami, *Curr. Sci.*, 1947, **16**, 182.
27. Mitra and Siddiqui, *Curr. Sci.*, 1948, **17**, 51.
28. Mitra, *J. Sci. Ind. Res.*, 1951, **10B**, 235.
29. Bhattacharji, Mitra and Siddiqui, *J. Sci. Ind. Res.*, 1949, **8B**, 188.
30. Amirchand, Mitra & Siddiqui, *J. Sci. Ind. Res.*, 1948, **7B**, 69.

31. Om Prakash, *Report, Indian Central Oilseeds Committee* 1950, December.
32. Ind. Central Oilseeds Committee, F. 7. Tech. (61)/51 dated 13.8.1951.
33. PTI News Item, *Hindustan Times*, New Delhi, Sept. 16, 1951, p. 7.
34. Dalal and Mehta, *J. Ind. Chem. Soc.*, (Ind. Edn.), 1939, 2, 213.
35. Mitra, *Ind. Pat.* No. 46713.
36. Bhattacharji and Mitra, *Ind. Pat.* No. 46947.

DISCUSSION.

Dr. N. G. Chatterji of the Hindustan Development Corporation Ltd., Calcutta, referred to the work carried out by Watson *et al* in 1923 resulting in the isolation of a crystalline compound and sulphur from the soap lye from nim oil. He further expressed that the sulphuric acid treatment of the oil could render it suitable for ordinary soap manufacture.

Mr. Om Prakash, oil expert to U. P. Govt., referred to some work carried out at the H. B. T. I., Kanpur with regard to the processing of nim seeds by the treatment of which the seeds could be kept for a year quite nicely, giving oil having less colour and odour. The process in the main consisted of three operations *viz.* (1) depulping (2) drying and (3) decortication.

Dr. N. N. Godbole, Director of Industries and Commerce, Rajasthan, stressed that the nim cake should also be put to some large scale use in order that nim seed crushing industry might be of maximum benefit. In this connection he suggested the possible utilization of the cake distillate as a denaturant. He further reported that nim seed were available in Rajasthan for Rs. 4 to 5 a maund and oil at Rs. 40/- a maund.

Mr. Mitra while replying to the above points remarked that 'margosopicrin' referred to by Dr. Chatterjee was perhaps analogous to 'neonimbidin' obtained during the hydrolytic degradation studies is nimbidin. Owing perhaps to the extremely labile nature of the bitter constituents and the inherent difficulties in working out their degradation products, characterisation of 'margosopicrin' did not appear to have been thoroughly carried out.

In regard to *ad hoc* treatment of nim oil with concentrated sulphuric acid, Mr. Mitra remarked that the acid while used for destroying the bitter constituents of the oil, would presumably affect also the glycerides to a considerable extent. Moreover, treatment of the oil with sulphuric acid could not possibly ensure total destruction

and removal of the bitter and the odorous constituents as the degraded products might not be water soluble or precipitated as charred mass. Such treatment would not only cause a considerable working loss in oil but the therapeutically active bitter principles which constituted valuable by-products in the scheme of utilization of the oil, would go waste when the oil also could not be obtained in desired quality.

In regard to processing of nim seeds, Mr. Mitra suggested that the ripe fruits should be depulped without being washed with water and they should be dried as quickly as possible to avoid the chance of auto-oxidation in the moist seeds during storage. Mr. Mitra further informed that the work on nim seed meal was in progress in the National Chemical Laboratory.

UTILIZATION OF *MOWRAH* OIL

BY

Dr. J. G. KANE

Department of Chemical Technology, Matunga, Bombay.

Newer oils are gradually coming under utilization. *Nim*, *Karanja* and *Kamala* may be cited as instances. What about new uses for oils which are already being utilized industrially? Attempts in this direction have opened up a vast field for investigation and yielded interesting products. We are now familiar with 'Modified' oils, which are also called 'Custom-built' or 'Tailor made' oils in the U. S. A. Fatty oils being mixtures of mixed triglycerides easily lend themselves to modification.

Mowrah oil, an indigenous fat with large annual production, is mainly used in soap manufacture. Its high colour, acidity and offensive smell make it unsuitable for edible purposes, although in Gujerat it is consumed for this purpose in small quantities. However, there is no reason why it cannot be converted into an edible fat after suitable refining.

Mowrah oil is characterized by the presence of a large proportion of palmitic acid in it. It has this characteristic in common with three other fats, viz., cacao butter, cottonseed oil and mutton tallow. A consideration of the fatty acid and glyceride compositions of the four fats as given in Table I brings out some interesting points. (Figures given in Table I are taken from the work of Hilditch and co-workers.)

TABLE I.

	Cottonseed oil	Mowrah fat	Cacao butter	Mutton tallow
I. V.	103-111	58-63	35-45	31-47
Acid composition, mol. %				
Myristic	2.0	—	—	5.5
Palmitic	21.2	24.1	24.3	26.2
Stearic	1.3	19.3	35.4	29.3
Oleic	29.6	43.4	38.2	34.8
Linoleic	45.3	13.2	2.1	4.2
Glyceride composition, mol. %				
Fully saturated	—	1.2	2.6	27.0
Mono-'Oleo'	12.0	27.8	76.8	31.0
(Oleopalmitostearin)	—	26.9	51.9	—
Di-'Oleo'	60.0	71.0	20.7	42.0
Tri-'Oleo'	28.0	—	—	—

Firstly, the number of component fatty acids is small. Secondly, all the four fats have the same fatty acids. Thirdly, the proportion of palmitic acid in all of them is similar. Thus the differences are only in the proportions of stearic and the two unsaturated acids. If the latter two acids could be straight away converted to stearic acid, it should be possible to prepare either cacao butter or mutton tallow from cottonseed oil or *mowrah* fat. However, two things go against this. The peculiar and characteristic properties of cacao butter are not so much related to its fatty acid composition as with its glyceride structure. In fact, cacao butter and mutton tallow are instances of how profoundly glyceride structure affects the physical properties of a fat. Therefore, mere hydrogenation will not convert *mowrah* fat into cacao butter, which was the main object of the present work. Hydrogenation will also tend to produce more of fully saturated glycerides. In addition, iso-oleic acids will be formed, the effect of which on the physical properties of the hardened product is difficult to predict.

Bailey and co-workers prepared cacao butter substitutes from cottonseed oil by hydrogenating it to an I. V. lower than that of the butter and crystallizing the product from acetone. The filtrate *i. e.* the more soluble part was found to be similar to cacao butter.

Mowrah oil has an obvious advantage over cottonseed oil. The degree of hydrogenation required will be less, and therefore, the amount of iso-oleic acids produced should be correspondingly smaller.

The experimental work comprised of the following stages:—

1. Refining.
2. Hydrogenation.
3. Solvent crystallization.

Refining :

Aqueous alkali refining, solvent alkali refining and esterification methods did not give satisfactory results because of the high acid value of the crude *mowrah* oil. Liquid-liquid extraction of the oil using ethyl alcohol of different concentrations was then studied and applied for the removal of free fatty acids. Using 90% alcohol at room temperature in the ratio of alcohol : oil = 4 : 1, three successive treatments reduced the acid value of the oil from 21 to 1.5. This oil was then deacidified by aqueous alkali.

Hydrogenation :

Using 1% Raney nickel or 0.5% wet reduced catalyst, rates of hydrogenation of *mowrah* oil were studied at 130°C. Straight hardened products having iodine values from 35 to 45 were tested for their melting range and micropenetration and were found to be similar to mutton tallow.

For the production of cacao butter substitute, the oil was hardened to a product of an I. V. 23 and m. p. 57°C. On analysis it was found to contain 6% iso-oleic acid, 71% saturated acids and 23% oleic acid.

Solvent Crystallization :

Several trials under different conditions with acetone and petroleum ether were made. With the latter solvent in the proportion of solvent : fat = 4 : 1 and at a temperature of 15°C, a precipitate and a filtrate were obtained in yield of 47 and 53 per cent respectively. The latter with an I. V. 37 and a fairly sharp melting point 41.7°C was found to be similar to cacao butter in its physical behaviour.

A detailed study of micropenetration, slipping points and melting points of cacao butter, the substituted mutton tallow and hardened groundnut oil was made.

The above is a report of preliminary work. Further detailed work is necessary to find out optimum conditions of hydrogenation and crystallization. It is also necessary to analyse the various products obtained for their component fatty acids and component glycerides.

DISCUSSION

Dr. M. B. Ichhapuria of the Tata Oil Mills Ltd., Tatapuram while commenting upon Dr. Kane's paper pointed out that 2-3 per cent of the unsaponifiable matter which would eventually remain in the soluble portion during crystallisation, would render it unfit for edible purposes. It was, therefore, necessary to remove the unsaponifiable matter as well as the free fatty acids by distillation before the fat was hydrogenated and crystallised for preparing cacao butter substitutes.

Dr. N. N. Godbole, Director of Industries, Rajasthan referred to the previous work on *Mowrah* oil carried out at the Benares Hindu University. In his opinion the high content (3%) of unsaponifiable matter made the soap obtained from the oil rancid very rapidly.

CATASTROPHIC INCREASE IN PRICE OF OILS AND OIL SEEDS.

BY

T. V. RAO, MANGLORE.

The purpose of this paper is to discuss briefly the present abnormal rise in the prices of oils and oil seeds with particular reference to edible oils and how far this spiralling increase has adversely affected both the *Vanaspati* and soap industries of this country.

Prior to World War II both the coconut and groundnut oils were sold at around Rs. 222/- per ton i.e. Re. 0-1-7 per lb., while *mowrah* oil was costlier by Rs. 90/- per ton. But today coconut oil is the costliest of all oils in India, being sold at Re. 1-2-3 per lb. Generally no industry can hope to survive unless its production costs are reasonable. Nor can any business continue to exist unless it is in a position to fix selling prices to the public on a competitive basis and at levels within the purchasing power of the general public. The present prohibitive prices of oils and fats make it difficult for the manufacturer to adhere to the above basic principles. While the prices of oils and fats go on increasing to a catastrophic level, the products made out of them are subjected to vexatious control leaving no margin at all for fair returns with resultant suffering of oil and kindred industries to a considerable extent. Consequently many *vanaspati* and soap factories have closed down and some are on the verge of being closed down and unless the Government takes up this matter forthwith and adopts a comprehensive price policy the situation is bound to prove disastrous at no distant date. Commodity prices and general values could always and needs immediate pegging at reasonable levels and it behoves Government to take steps in this direction in consultation with economists. That is the only course which when undertaken is sure to go a long way to protect industries from the gyrating raw material prices.

Let us now examine whether our prices of oils and fats compare well with those prevailing in foreign countries. The industrial backwardness of India coupled with the economic poverty of her people ought to have, as one should expect, kept the prices of oils and fats at low level, lower than the prices prevailing in the United Kingdom. But to our dismay it has not been so. In England today coconut oil is the cheapest available raw material for industry being

valued at 12 annas per pound. Undoubtedly this is because of Britain's trade monopoly over the copra producing colonial countries. It is of interest to note that linseed oil is the cheapest available oil in India, but still costlier than in U. K. while it is the costliest in England.

When we compare the price of oil and fat in India and United Kingdom, we find that we are paying an abnormally higher price in India (Table I). For example, we pay Rs. 860/- per ton more for coconut oil than what is paid in England. Similarly, groundnut oil costs us Rs. 387/- more per ton and sesame oil costs us 410/- more per ton and linseed oil is costlier by Rs. 60/- per ton than in England.

TABLE I
THE COMPARATIVE OIL AND FAT PRICES IN INDIA
AND UNITED KINGDOM.

(Exchange Rate: 1 £. = RS. 13.3)

Oil and Fat.	Price per ton in			Excess cost in India over that of UK p/t.
	India.	United Kingdom.		
	Rs.	£.	= Rs.	Rs.
Coconut oil Crude	2,540.	126	1,680	860.
Groundnut oil „	2,120.	130	1,733	387.
Sesame oil „	2,120.	120	1,710	410.
Linseed oil „	1,980.	144	1,920	60.

Assuming the yield per acre of cultivable land as the basis for determining the cost of oils and oilseeds, the position would be entirely different. Supposing the annual yield of crops and acreage under production is tabulated and the price of oils and oilseeds worked out on the basis of a standard revenue return per acre of say Rs. 200/- per annum is fixed for all crops, then we find that while 1 cwt of sesame seed costs round about Rs. 38/-, actually it should be valued at Rs. 192/- per cwt based on Rs. 200/- income per acre crop (Table II). Happily the groundnut market cost and the standard yield of Rs. 200/- per acre tally with its ruling market price of Rs. 48/- per cwt. Similarly, linseed market price per cwt should be Rs. 96/-, while it is sold at around about Rs. 44/- per cwt and castor seed should be valued at Rs. 144/- per cwt as against market price of Rs. 47/- per cwt. It may, however, be admitted that groundnut is a full crop while sesame, linseed and castor are mixed crops with cotton etc., and hence the different rates for different crops as is

TABLE: II

Oil Seeds	Acres 000	Yield Tons 000	Cost per cwt. of seeds Rs.	Yield per acre		Cost of seed per cwt based on Rs. 200 annual return per acre. Rs.
				Seeds lbs.	Value Rs.	
Sesame ..	4,502	322	38	160	64	192
Groundnut ...	10,272	4,099 (Unshelled) 2 460 (Shelled)	48	464	199	48
Linseed ..	3,400	425	44	252	99	96
Castor ..	1,781	100	47	160	67	144
Coconut (In Nos.) ..	1,500	30,00,000	18	2,000	360	10

prevailing are justified. But in the case of the coconut, we have not only a full time but also a recurring crop with its innumerable advantages. Its leaves, husks, shells etc., which are used industrially and domestically and so it fetches a far higher return to the owner than the groundnut, linseed or castor plants. If the coconut revenue is to be levelled to that of an average of Rs. 200/- per acre, each coconut could be valued at *not more than 1 and 1/2 annas* and the coconut oil would cost us approximately Rs. 1,300/- per ton or 50% of the current rate and no more. This figure would be reasonably within the world coconut oil prices.

In so far as the soap value of oils and fats is concerned it is an admitted fact that coconut oil is indispensable to the soap manufacturer though tallow, hydrogenated vegetable and fish oils etc. are often used. While groundnut oil soap is softer in consistency and so unfit for hard soaps, it is costing 1 and 1/2 annas per lb. more than soap made from Australian tallow which is naturally preferred. And by using hydrogenated groundnut oil in place of Australian tallow the economy in soap cost is upset by *not less than* Rs. 0-2-10 per lb. of pure soap manufactured. If, however, the 1950 production figure of 60,000 tons of soap is manufactured from 15,000 tons of animal tallow in place of normal usage of hydrogenated vegetable tallow then (Rs. 0-2-10 x 15,000 tons x 2,240 lbs) = Rs. 5,19,50,000 will be saved by the soap makers. And there is also the other possibility of the groundnut oil price decreasing to the lower limits of this animal tallow

price by such industrial psychology. It is a pity that India has not at all advanced in this industry while Australia has perfected the animal tallow industry.

When we look into the various index price of cost of living (Table III), we find that while cost of living has stood at 300% above the pre-war level, the pure *ghee* index price has increased to 400%, the soap index price base increased by 425% where as the index price of groundnut oil has gone up to 960% and that of coconut oil has gone up as high as 1,155%. What a disparity in price !

TABLE III.

Particulars	Average price per ton & living index		Percentage increase over 1938	1938 groundnut oil price being Rs. 0-1-7 per lb. to-day's price per lb. must be only.			To-day groundnut oil price per lb. @ Rs. 0-15-3 each excess in India per lb. by		
	1938	1950		Rs.	As.	p.	Rs.	As.	p.
1. Index Number of :									
(i) Cost of living ...	100	300	300	0	4	9	0	10	6
(ii) Mineral and other industrial raw materials ...	100	350	356	0	5	3	0	10	0
(iii) Fibres ...	100	350	350	0	5	3	0	10	0
(iv) Oil seeds ..	100	650	650	0	10	0	0	5	3
2. Oils and Fats Price :									
(i) Pure Ghee ..	1680	6720	400	0	6	4	0	8	11
(ii) Groundnut oil.	222	2120	960	0	15	3	...		
(iii) Coconut oil....	222	2540	1155	...			..		
3. Washing soap.	400	1700	425	0	6	9	0	8	9

The present uneconomical prices level of raw materials are due to the appalling breakdown in planning as follows :— Firstly, if the Government had not imposed high import duty of Rs. 500 per ton on coconut oil; secondly, if the Government had not controlled the price of finished product *Vanaspati*, while the price of raw material, groundnut oil, goes on increasing unchecked, and thirdly, if the Government had not been unconcerned over the imported oil prices in rupee value which should be reduced by 30 per cent, the present catastrophic increase in price of oils and oil-seeds could not have occurred and the crisis in *Vanaspati* and soap industry would have been averted.

It is hoped that the Government would reconsider the above points and exercise an effective check over the increase in prices of oils and oil seeds and thus give an incentive of good return for *Vanaspati* and soap industries at an early date.

DISCUSSION

Mr. S. C. Gupta informed about the experiments conducted in the National Chemical Laboratory on Pisa seed fat as substitute for coconut oil in soap making.

Dr. S. A. Saletore, Asst. Director, Central Laboratories, for Scientific and Industrial Research, Hyderabad and **Dr. M. B. Ichhapuria** of the Tata Oil Mills, however, pointed out the non-availability of Pisa fat in commercial quantities. The firm of Dr. Ichhapuria could not get even three tons of this fat for their experimental purposes.

Mr. Gupta was still of the opinion that the production of Pisa fat could be increased if the forest people might take active steps in the matter. Hydrogenated rosin was also found to replace partially coconut oil in soap making.

Dr. J. G. Kane of the Bombay University informed that the Bombay Government found the cultivation of Pisa seed as uneconomic.

Mr. I. M. Qureshi, silviculturist, Bombay State stated the supply of Pisa seeds was very limited. The tree grows mainly in the districts of Mahabaleshwar, West Khandesh, Dharwar and Hubli. It takes a long time of 15 to 20 years to fruit and so the only thing that was possible was to conserve the Pisa trees so that with time they might multiply.

Mr. T. V. Subba Rao of the Tata Oil Mills emphasized the employment of less known non-edible oils in soap making.

Dr. N. N. Godbole Director of Industries and Commerce, Rajasthan pointed out that the soaps made from hydrogenated oils were very good in look, body and consistency but they were very poor in lathering properties. He put the Government of India to a great extent responsible about the difficulties of soap industry as regards the high prices of coconut oil which was due to the export duty on this oil by Ceylon Government on one hand and an import duty levied by the Government of India on the other.

Mr. G. M. Kelkar of the Village Industries Laboratory, Poona pointed out the drawback of high free fatty acid in *Mowrah* oil as a result of which it could not be used in high grade soaps. He, however, suggested that for improving the lathering properties of soap prepared from hydrogenated oils, such fats could be blended with some natural oils.

Dr. N. G. Chatterji of the Hindustan Development Corporation, Calcutta informed that during the last four years they had supplied about 400 tons of hydrogenated groundnut oil to a big soap factory and its use had decreased the consumption of coconut oil at that place.

Dr. Aggarwal (N.C.L.), however, pointed out that the importance of coconut oil in soap is due to the high amount of lauric acid that it contains and therefore it can not be substituted by hydrogenated groundnut oil. It was due to that reason that Mr. Gupta mentioned the use of Pisa fat in soap making which contains about 96 per cent lauric acid.

OIL AND ALLIED INDUSTRIES IN THE FUTURE DEVELOPMENT OF INDIA.

BY

P. K. PATNAIK

Special Officer, Oil Cooperatives, Government of Orissa, Bhuvaneshwar.

The naturally occurring oils are not only themselves very useful, but also form raw materials for a wide variety of industries, and enter into our daily life at many places. Things such as toilet and washing soaps, cosmetics, food products, paints, polishes, lubricating oils, confectionery etc. have become almost indispensable.

The natural oils are divided into three main groups (i) Mineral oils (ii) Essential oils and (iii) Fatty oils.

Mineral oils.

The first group comprises Petroleum and its homologues. India is very poor as regards mineral oil deposits. As these oils find use in the internal combustion engines, we shall have to look up for a substitute. For this, production of power alcohol from molasses must be given due emphasis. The possibility of hydrogenation of Indian coal for petrol needs careful consideration.

Essential oils.

The essential oils are contained in the flowers, leaves, stems of plants. India's essential oil trade can be known from the following figures. (All the figures in this paper relate to a period of 7 months from 1-4-1946 to 31-10-1946 of undivided India, unless otherwise stated).

About 74 lakhs of rupees worth of various crude essential oils and 72 lakhs of rupees worth essential oil bearing materials were exported from India, and total import of essential oils was about 47 lakhs of rupees worth.

The crude essential oils under their genuine names are exported to foreign countries and we import the very same products with certain modification under trade names. The essential oils industry of India is very old, and it is expected that if due care is given, this industry will flourish in no time.

Fatty oils: India's trade in oil seeds.

Export of oil seeds from India from (1-4-46 to 31-10-46) was 2,17,282 tons valued at 3,69,53,207 rupees; major items of the export

were groundnut, linseed and castorseed. The import of oil seeds from abroad amounted to 3,150 tons of copra from Ceylon during the same period.

India's trade in oils:

Export (from 1-4-46 to 31-10-46) was nearly 9,62,000 gals. of fatty oils amounting to about 46 lakhs of rupees.

Import (from 1-4-46 to 31-10-46) was as follows :—

Fish oil : 34,800 gals. valued at Rs. 1,56,500

Coconut oil : 27,23,978 „ „ 91,45,804

Total „ 93,02,304

India's trade in oil cakes:

Export 47 tons (mainly rape and sesame)

Import 4 tons.

Oil crushing industry in India.

This industry forms the basis of the oil and allied industries. In India there are about 3,000 big oil mills but the old village *ghannies* still continue to be the most important oil crushing machine. The cost of *Ghannie* process is more than three times the cost of milling by modern machinery. Not only there is a reduction of cost, but there is a decided advantage in the total output and yield. Practically one expeller can produce during one day as much as one *ghannie* can produce during one whole year.

The demand of oil for edible and industrial purposes is far below the average, and large quantities of seeds are being exported every year.

The failure of not crushing all the seeds is due to want of technical and commercial knowledge on the part of management, and failure to recognise the necessity of erecting only the best and most modern machinery and of securing efficient scientific control, and lack of production of best and the most efficient machinery in the country.

Edible fat Industry of India:

In India, edible fats are clarified butter (*ghee*), mustard, sesame and groundnut oils mainly, though people of some parts use coconut oil, fish oil, etc. India's production of oils and fats, however, for edible purposes, is far below the normal requirement.

India's production of edible oils 12,71,000 tons/annum (5 years average, ending 1944-45)

—do— *Ghee* & Butter 8,17,000 tons/annum

Total : 20,88,000 tons/annum.

According to the balanced diet estimate the requirements of oil and fats for food, in Indian Union, having a population of about 350 millions, with two bare diets per head a day, amounts to about 10 million tons per annum. Considering the present production of edible fats in India, we are already short of about 70 lakh tons of oils and fats.

The *Vanaspati* Industry:

There are 60 hydrogenation factories in India with an installed capacity of over 4 lakh tons of *vanaspati* and about two dozen oil refineries producing 60,000 tons of refined oils per annum. The *vanaspati* factories are also producing refined oils. The total production of refined oils is 1,20,000 tons of which 95,000 tons are groundnut oil, 10,000 tons coconut oil and 15,000 tons cottonseed oil.

Soap trade in India (1-4-46 to 31-10-51) :

	Quantity.	Value.
Export:	1,067 tons.	Rs. 15,78,997/-.
Chief customer of Indian soap is Iraq.		
Import:	Mainly from U. K. and U. S. A.	(1-4-46 to 31-10-46)
	Household & Laundry soaps.	21.6 tons.
	Toilet soap.	55.5 tons.
	Other kinds of soap.	29.5 tons.
	TOTAL	106.6 tons.

Production of soap in India during the year ending 1944-45 was 32,48,000 tons, in about 120 big soap factories. But the *per capita* consumption of soap in India is 12 oz as against 25 lbs in U. S. A.

Paint and Varnish Industry:

There are about twenty big paint and varnish factories in India located around Calcutta and Bombay.

India's export of paints and painters' materials. (1-4-46 to 31-10-46).

	Value
Turpentine.	Rs. 10,568
Other sorts.	Rs. 10,02,208
TOTAL	Rs. 10,12,776

India's import of paints and painter's materials (1-4-46 to 31-10-46) is of pigments amounting to 84,173 cwt. valued at 61,78,799 rupees. Major items are Paris blue, zinc white and lithopone.

Painter's materials other than pigments:

	Quantity (Cwt.)	Value (Rs.)
In 1945 for the } Turpentine (Genuine)	1,265	9,600
same period. } Turpentine (Substitute)	75,130	4,61,139

TOTAL 4,70,739

Besides some special types of varnishes, lacquers and enamels are also imported.

A few years back India was importing boiled linseed oil for the paint industry. But now the boiled oil requirement is met from production entirely in India. Though India's forests are a rich source of varnish making materials, and the country is rich in minerals for manufacture of pigments, still India imports about one crore rupees worth of paints and painters' materials.

Glycerine industry:

Glycerine is the common constituent of all fixed oils and fats, and hence this industry is closely associated with the oil and fat industries.

About 5 per cent of glycerine is associated with all fixed oils and fats. In India, although more than 30,00,000 tons of soap is produced annually, very little glycerine is recovered at present and hence about 2,70,000 tons of glycerine is being wasted annually. It debars the opening up of so many new industries particularly cosmetic industry.

India imports cosmetic products worth two crores of rupees annually.

Fat Splitting:

Glycerine can also be obtained by splitting of fats. The fat splits into its two constituents: glycerine and fatty acids. The fatty acids may be used in soap and candle making, so that glycerine can be made available for the numerous other preparations.

Candles worth about 16,000 rupees are imported into India annually.

Lubricants:

Formerly, the mineral oils monopolised this industry. But now it has been proved that in some cases properly treated vegetable oils are better suited.

The vegetable oils are suitable lubricants from the bullock cart to the high speed aeroplanes. It is said that castor oil is a necessity in any plane flown to a great height, because the oil has the very important flowing quality at very low temperature and when it is partially dehydrated it becomes miscible with mineral oils. The oil does not eat away the gaskets, hence is a perfect oil for hydraulic brakes. Blown mustard oil is also used for lubrication purposes.

Wax Industry :

India exports about 20,000 tons of paraffin and other waxes annually and imports polishes like leather polish, wood polish, metal polish, prepared from the waxes, worth about 50,00,000 rupees.

Linoleum Industry :

Most of India's requirements of linoleum are imported though it is the land of linseed oil, which forms the basic material of this industry. It is gratifying to note that very recently a linoleum factory has started working at Calcutta.

Confectionary :

Cacao butter fat is used in chocolate manufacture and fats of this group are found in the fruits of Indian *sal* tree, '*Shorea Robusta*'. The possibility of application of this fat in confectionery has to be explored.

The task ahead :

India's production of oils is short by nearly seventy lakh tons, calculating on the basis of 1.5 oz. per head, per day for edible purposes. The task of meeting this shortage should be taken up immediately by the Government. Cultivation of oilseeds does not hamper the production of cereals as the former is raised on lands not quite suitable for the latter or as a second crop. Moreover, addition of fats to the cereal diet diminishes the quantity of cereals without affecting the total calorific value of the diet. In view of this fact, production of oilseeds should receive top priority in the food production drive.

PRODUCTION AND UTILISATION OF MUSTARD OIL IN INDIA.

BY

OM PRAKASH,

Oil Expert, Govt. of Uttar Pradesh, Kanpur.

India is a large and important producer of rape and mustard seeds. Of the total output of about 6 million tons of oilseeds in India, production of rape and mustard seeds is about $3/4$ million tons which ranks next only to that of groundnut. Although the production of cottonseed is higher than that of mustard seed, being about 1 million tons, yet it is not of much importance as an oilseed for the present, as the crushing of cottonseed in India so far is only negligible.

There are several species of rape and mustard seeds grown in India, the chief being :—

- | | | | |
|-------|---|---|---|
| (1) | <i>Brassica campestris</i> , yellow variety | : | known in vernacular as <i>Pili sarson</i> . |
| (2) | „ „ brown „ | : | known in vernacular as <i>lal sarson</i> . |
| (3) | „ <i>juncea</i> Rai | : | known in vernacular as <i>lohi</i> . |
| (4) | „ <i>napus</i> | : | known in vernacular as <i>toria</i> . |

Oils from the pure varieties of these seeds are very similar to each other and have only slight differences in their physical and chemical characteristics. But the mustard seed of commerce available for crushing is generally a mixture of different species in varying proportions. This is due to the fact that the seed itself which is used by the agriculturist for sowing purposes consists of a mixture of various species. The result is that oil millers cannot get pure seeds of any single *Brassica* species but have to purchase mixtures of different species. Slight variations in the physical and chemical characteristics of mustard oil of commerce are, therefore, natural and depend upon the mixtures of seeds crushed.

Besides the seeds of the *Brassica* family, there is another species of seed which gives an oil similar to the oil of the *Brassica* family. This species is *Ernca sativa*.

Rape and mustard seeds are grown from August to November and the crop is harvested from January to April. The area under cultivation and production of these seeds are given in the Table I.

TABLE I.

Acreage and production of mustard and rape seeds in India.

Period	Acreage '000 acres.	Production '000 tons.	Export out of India '000 tons.	Available for local con- sumption '000 tons.
From 1901 to 1910	5,827	1,001	—	—
From 1911 to 1920	6,292	1,149	174	975
From 1921 to 1930	6,023	1,036	159	877
From 1931 to 1940	5,304	893	55 ¹	838
From 1941 to 1948	4,328	782	·047 ²	782

1. Average of 7 years from 1930 to 1937.

2. Average of 3 years from 1946 to 1949.

Average world production of rape and mustard seeds during 5 years 1941 to 1946 was 3,641,000 tons, China being the largest producer with a production of 2,274,000 tons. India thus produces about 22 per cent of the world supply of rape and mustard seeds. Practically the whole of the production of the seed is consumed within the country. The average yield of seed per acre is less than 400 lbs. whereas the yield in Germany is from 1200–1600 lbs. per acre.

Importance of rape and mustard seed among the various oilseeds produced in India can be realised from Table II.

TABLE II.

Average production of oilseeds in India (Indian Union).

Name of oilseed	Average annual production during eight years 1941–1949. (tons)
Groundnut	33,26,000
Cottonseed	11,00,000
Rape & Mustard	7,70,000
Sesame	3,62,000
Linseed	3,87,000
Castor	1,49,000

Average acreage and annual production of rape and mustard in various parts of Indian Union during the 4 years (1945 to 1949) is given in Table III.

TABLE III.

State	Acreage in '000 acres	Production in '000 tons.	Approximate % of total production.
Uttar Pradesh ...	2829 (both pure & mixed crops)	489	63
Bihar ...	478	97	12
Punjab ...	347	50	6.5
Madhya Pradesh ...	156	27	3.5
West Bengal ...	142	26	3.5
Matsya ...	120	16	2
Madhya Bharat ...	73	10	1
Bombay ...	33	5	0.5
Vindhya Pradesh...	49	4	0.5
Orissa ...	27	5	0.5
Hyderabad ...	5	less than .5	—
Delhi ...	4	„ „ .5	—
Rajasthan ...	6	1	—
Total ...	4,581	781	

It will thus be seen that of the total production of rape and mustard seeds in India, U. P., produces about two thirds and U. P., Bihar, Punjab and Assam together produce about 90 per cent.

Of the total quantity of rape and mustard seed produced in India, its utilization is roughly as given in Table IV.

TABLE IV.

Seed Produced	Seed used for sow- ing @ 5%	Seed used for domestic purposes @ 10%	Balance used for crushing	Oil produced	Cake produced
(tons)	(tons)	(tons)	(tons)	(tons)	(tons)
7,82,000	39,000	76,000	6,67,000	2,22,000	4,32,000

As regards inland trade in mustard and rape seed the main features are that exports of seed are chiefly from U. P., Punjab, Rajasthan, Madhya Pradesh, and Madhya Bharat and the chief importing States are Bengal, Bihar and Assam.

As stated above about 667,000 tons of mustard seed are crushed in the country yielding about 222,000 tons of oil and 4,32,000 tons of oil cake. Mustard oil is almost exclusively used as an edible oil, being a favourite oil in certain parts of India such as Bengal, Assam, Bihar, and Orissa and also in Eastern Pakistan. It may be safely said that over 95% of the oil produced is used for edible purposes, the rest being used for massaging the body, as hair oil and as burning oil and sometimes for industrial purposes such as preparation of blown rape oil for lubrication purposes. The oil cake obtained is used as cattle feed for which purpose it is highly valued. Practically the whole of the oil and oil cake produced are used within the country. It is estimated that about 50 per cent of the seed, available for crushing, is crushed on cottage industry scale in bullock driven *kolhus* or *chakkus* and the remaining 50 per cent is crushed in power driven mills of varying sizes and with more or less modern appliances.

As already mentioned, the State of Uttar Pradesh produces about two thirds of the total quantity of mustard and rape seed produced in India, with Bihar coming next with only about 12 per cent production. Uttar Pradesh is thus a surplus area with regard to the production of mustard and rape seeds and supplies the needs of mustard oil consuming areas such as Bengal, Bihar, Assam, Orissa and Eastern Pakistan. Its position, therefore, in the production and crushing of mustard seed is unique. Of the total production of mustard seed in U. P. viz about half million tons, over 60 per cent. i. e. one third million tons are crushed within the State which gives over one hundred thousand tons of oil. One third of the total oil produced i. e. 33,000 tons is exported out of the State. This 33,000 tons of mustard oil exported out of the State is the production of large scale oil crushing industry of U. P. The balance of oil i. e. about 67,000 tons is produced partly by the cottage oil industry by the bullock driven *kolhus* and partly by the small oil mills run by power driven *ghannies*. It will, thus, be seen that the large scale industry of the State depends to a large extent on the export market of mustard oil. This can be further seen from the fact that of the total production (over 9,00,000 tons) of oilseeds in U. P., mustard seed forms over 50 per cent, linseed and sesame coming next in order of production with only 15 and 12 per cent respectively.

It can thus be seen that the mainstay of the oil crushing industry of U. P. has been mustard seed crushing and that crushing of linseed, sesame, castor, groundnut, mahua are of secondary importance. The oilseed crushing industry of U. P. has expanded during the last two decades during which period it established markets outside the State for its chief produce viz. mustard oil; chief markets

being West Bengal, East Bengal (which now forms part of East Pakistan), Assam, Bihar and Orissa, the first two taking up the bulk of the supply. During the second world war, when there was a shortage of mustard oil, the supply of mustard oil to consuming areas was under Government control and over 10 lac mds. of mustard oil used to be supplied annually by U. P. oil millers through the U. P. and Bengal Governments. But since the close of the world war and the partition of the country, the position has somewhat changed; firstly on account of the shrinkage of the market for mustard oil due to East Bengal having gone over to Pakistan and secondly on account of the natural tendency of different States of India to try to become self-sufficient as far as possible.

Apart from the above changes a serious obstacle in the way of the mustard oil industry is the diversity of specifications of mustard oil drawn up by various State Governments and the different Departments of the Central Government, due to which the industry has suffered much during recent years.

The various specifications at present existing in India are as given in Tables V and VI.

TABLE V

Specification laid down by	Saponification value	Iodine value	Other characteristics.
Bengal Govt. Ref. No. 1977 P. H, 24-7-40 ...	169-175	96-104	
Bihar Govt. Ref: No. 9363 L.S.G.Dt. 16-12-1924 ...	169-176	96-108	
U. P. Govt. Ref: No. 1037/XVI (P.H.)-322 Dt. 22-12-1930 ...	169-176	96-108	
Madhya Pradesh Govt. ...	169-176	96-108	
East Punjab Govt. Ref: No. 7202 P.H., Dt. 10-12-31 ...	170-180	93-105	
Govt. of India, Ministry of Ind. & Supplies (I.S.D.) G.O. 101/73 (1937) ...	170-178	93-108	Acid value not more than 6.0 sp. gr. at 30°C/ 30°C. 905-.909.

TABLE VI

	Sap. value	Iodine value	Refractive index at 40°	Sp. Gr. 30/30	Unsap matter %	A.V.	Natural Essential Oil. %
Govt. of India, Ministry of Agriculture ... (Agmark Special grade) ...	170- 175	99- 106	1.4646 1.4666	.905- .908	1	2	.4 to .75
(Grade A) ...	170- 176	98- 106	1.4643 1.4669	.905- .909	1.5	4	.3 to .75

This anomaly on account of the difference in the various specifications is a great handicap to the mustard oil industry as the oil which is genuine and pure and satisfies one specification may be declared as adulterated when compared with another specification. During recent times certain authorities have not only rejected mustard oil falling slightly outside their rigid specifications of iodine or saponification values while falling within the ranges of other specifications but have also prosecuted the supplying firms for adulteration on the basis merely of slight differences in iodine or saponification values without establishing the presence of any adulteration. This places the mustard oil industry in a serious situation and calls for suitable action for its amelioration. On the one hand, it is desirable to have uniform specification for edible mustard oil throughout India and on the other hand it is worth consideration whether to prosecute a firm for sale of adulterated mustard oil. Should it not be necessary to carry out extra tests for establishing adulteration besides doing a single test for saponification or iodine value. It is one thing to reject a supply not coming up to a certain standard and another thing to prosecute a person for selling adulterated stuff. It stands to reason that in the latter case either the deviation from the specification limit should be well beyond the tolerance allowed for such tests or extra tests for establishing adulteration should be performed.

TRADING IN VEGETABLE OILS IN INDIA AND ITS FUTURE.

BY

TULSIDAS M. VISHRAM,

Hon. Secretary, Oil Merchants' Chamber Limited, Bombay.

Since ages, vegetable oils have been one of the principal nourishing sinews of human system and have recently emerged in modern times as important ingredients in industrial activities. India has since long been one of the leading oilseeds producing countries in the world and occupies a prominent position in world trade in oilseeds and oils. Along with other primary professions sustaining human life, extraction of oils from oilseeds has been an ancient profession in India though may be initially through crude means and methods. It is said that India exported sesame oil to East African Coast as long back as 60 A. D.

It, however, appears that rapeseed oil (*Sarsav* oil) was almost the first oil to enter into trading in India, which has been carried on right from Vedic times. Even now rapeseed oil is widely consumed in Uttar Pradesh, Bengal, East Pakistan, Bihar and other areas. There exists a popular fallacy arising from confusing nomenclatures of rapeseed and mustard seed. Rapeseed ought to be known as *Sarsav* and not as *Rai*, which really means Mustardseed. Rapeseed is an oilseed while mustard seed is really speaking not an oilseed but a condiment, a sort of spices, with very little oil content, which has medicinal uses. Sesame oil, offering better use and taste for culinary purposes, gained importance in trading later on, preferably during last thousand years or so. It had all along maintained its position but in present times its place has been taken by groundnut oil, due to increasing use of the latter. Coconut oil was the next important oil to come under the sway of trading in India. It has been widely used for edible purposes in South India and as hair oil and for toilet purposes in other parts of India. Soap manufacture has however recently commenced to claim this oil in increasing volume as its basic raw material. Coconut oil has all along maintained its position in oil trade in India and has been put to various uses. Linseed oil and castor oil were the next oils in importance to become articles of trading, the former due to its suitability in manufacture of paints and varnishes and the latter first as an illuminant and secondly as a

lubricant, vital for industrial operations. Trading in groundnut oil is comparatively speaking of later origin, though it can now claim to be the King of oil and by its sheer volume due to increasing use both for consumption and industrial purposes including hydrogenation has now come to dominate the entire sphere of trading in oils in India. India also occupies the leading position in world trade in groundnut oil. During pre-partition period, cottonseed oil figured appreciably in trading in India but the creation of Pakistan has planted the major portion of cottonseed oil industry within its confines as the bulk of cotton producing areas has been included therein. *Mahuwa* oil, used mostly for soap manufacture but also partly as edible oil in producing regions is the next oil in importance, followed by Safflower seed oil and Niger seed oil, which are both used as edible oils mostly in producing areas. Trading in essential oils as distinct from vegetable oils is neither so voluminous nor so organised as the latter. Qualitative improvement as well as finding more and better uses for essential oils would offer greater scope for developing both our internal as well as export trade in these oils.

India's trade in vegetable oils has passed through many vicissitudes during the last century. Inter-state trade in these commodities commenced within the country from the beginning of the 20th century. Oil crushing industry has its roots as an indigenous cottage industry and was thus mainly confined to villages. Consequently trading in vegetable oils was also more or less a rural affair until the advent of railways, power crushing oil mills, soap industry, etc.

Next to *ghee*, edible oils occupy an important position in Indian diet imparting nourishment and thus they were always in greater demand due to their manifold requirements. The crushing industry, however, emerged as an important industry from its confines of indigenous industry only during the last 25 years and has thus given fillip to the trade in oils in our country.

Apart from other difficulties, viz., technical know how etc., the trade in vegetable oils primarily suffered on account of the lack of any centralised agency or regional associations to organise and regulate it on sound commercial basis. Of late this has been to a greater extent remedied and in the course of last few years, several well-organised commercial associations have come into existence on regional basis and are efficiently functioning in principal centres of trade in different parts of the country, viz., Bombay, Madras, Calcutta, Delhi, Rajkot, Cochin, etc. No substantial measure of progress had been so far achieved on all-India basis, but this lacuna has now been removed with the recent formation of

the Central Organisation for Oil Industry and Trade which has come into existence subsequent to the all-India Conference of Associations of oil Industry and Trade held in Bombay in July 1950. During the span of an year or so of its existence the Central Organisation has directed its attention towards varied problems confronting the oil industry and trade and one would wish and hope that it may render much-needed services to the trade and industry on countrywide basis. The oil trade and industry has not received the motherly treatment which it ought to receive from the Indian Central Oilseeds Committee and this leaves much to be desired and improved.

Trading in vegetable oils is not usually of a complicated character. Prior to second world war, business in oils was carried on subject to the conditions that oil offered for sale should be free from rancidity. Such crude and elementary methods for trading are now more or less a matter of the past in principal centres of oil trade and trading practice has undergone certain welcome changes. With the growth of *Vanaspati* industry consuming groundnut and other oils in considerable proportions, their entire trading has been on the basis of analytical tests in laboratories and the wholesale trading in oils is now being carried on more or less the same pattern of analytical findings in the laboratories of commercial associations regulating this trade. But the mercantile class has on the whole not as yet been fully acquainted with nor adjusted itself to the necessity and utility of analytical tests and other technological processes in their business dealings, with the result that where goods of superior quality might be needed, they at time send the goods of inferior quality and where the latter may serve the purpose, they even send the former. Further the business people due to their inexperience of technical knowledge, are not as yet in an assuring position to offer technological suggestions for substitutes in place of such oils which may either be unobtainable in or untransportable to particular regions and areas. This cannot indeed be considered a happy state of affairs but the technologists as a class can also to a certain extent be considered to be responsible for these conditions. They seem to have so far kept themselves studiously aloof from the main springs of commercial activity. They cannot afford to remain as mere academically interested onlookers but should actively associate themselves with the commercial community, and lend them the co-operative weight of their technological knowledge and experience towards the solution of many technical and allied problems confronting them. The business people on their part shall have to actively cultivate their consciousness towards things technological and avail themselves of their knowledge and experience to the utmost in their trading activities. There are a variety of oils produced and

consumed in different parts of the country and having varied industrial uses. Naturally trading in oils is both voluminous and spread all over the length and breadth of the country. The total annual turnover of the vegetable oil trade would be about 10 lacs of tons, valued at Rs. 200 crores. This trade entails movements of oils from producing centres to consuming centres and terminal markets in considerable proportions. It is computed that as much as 3 to 4 per cent oil valued approximately at Rs. 7 crores at current market rates is annually wasted due to leakage in transit on account of faulty containers, which are mostly the modes and means of transporting oils. This is sheer national waste, which though avoidable, yet for the present unnecessarily tends to swell the cost structure of oils. The question of packing is thus very vitally connected with the progress of oil trade but it is indeed unfortunate that this problem has not yet met with any satisfactory solution as would eliminate this wasteful leakage. The technologists have before them a very important task in this respect and they would be rendering a lasting service to the oil trade and industry by finding out suitable means and methods as would facilitate bulk transport of oils without the resultant leakage. Greater provision of more tank wagons and erection of oil storage tanks of various sizes both at principal centres of production and terminal markets by railway administration can be expected to be of some help in bulk transport of oils for internal trade of country but that would not to my mind thoroughly solve this vital question of containers.

Absence of standard contract terms for vegetable oils having universal application all over the country is one of the major handicaps of trading in these commodities. It is of the utmost importance that the Indian Central Oilseeds Committee should expedite evolution of standard contract terms for various vegetable oils in consultation with commercial organisations concerned and see to it that they are adopted by the trade oil over the country. *Vanaspati* manufacturing factories owned by foreigners, have so far by the virtue of their position as bulk purchasers of oils, been in a position to dictate their own terms of trading to our business people. It is indeed high time that they fall in line with India's Commercial Community and Organisations interested in oil trade and industry. Care shall, however, have to be taken to see that with a view to providing incentive for qualitative improvement of goods, the crushers or sellers should be enabled to receive some premium for better quality goods. This, however, is not the position at present as there is not reciprocal contract in force amongst the oil trade and hence its necessity.

Oil is at present sold either by measure or by weight. When sold by weights, it differs from place to place all over the country even at times the weight known by same nomenclature, viz., maund, khandi, etc., have different weight-contents in different parts of the country. This lack of uniformity of weights hinders the adoption of uniform quotations all over the country which would otherwise highly facilitate the trade as well as the consumers in general. The Government of Bombay have recently introduced weights of Maund and Seer series for oil trade but uniformity on all India basis is all that is needed.

Unsteady and vacillating policy pursued by the Central Government regarding export of oils and oilseeds has been most unhelpful to the trade. The system of allocation of export quotas leads to unnatural conditions, and militates against healthy functioning of the trade. It has now been acknowledged by all hands that exports of oils should be preferred to exports of oilseeds. This would give necessary impetus to our crushing industry and provide the country with valuable stocks of oilcake. However, the absence of tanker facilities in the steamers as well as oil storage tanks of suitable sizes at all the ports handling exports of oils in bulk, is another major handicap adversely affecting our export trade in vegetable oils.

While we have observed the position of oil trade in our country a word about trading in foreign countries would not be out of place. Excluding groundnut oil, linseed, castor oil etc., palm oil, olive oil, soybean oil and cottonseed oil are some of the prominent oils produced in various foreign countries and these oils enter into world trade in considerable proportion. As a result of their advance in technical knowledge and progress in scientific research, the Western countries have been able to make notable strides in the sphere of crushing industry and trading in vegetable oils. Their methods of storage and transportation of oils, research work for quality improvement leading to greater yield of oil etc., should indeed be considered worthy of emulation.

In the context of our post-partition national economy, the oil trade as well as industry will have an honoured and valued part to perform for raising and enriching the standard of living of our teeming population. It is gratifying to note that amity exists between the crushing industry and oil trade which are but two vital adjuncts of a valued sector of our national economy. But efforts shall have to be made to bring them still closer and completely harmonise their mutual relations and inter-dependence in terms of complete trust and understanding amongst themselves. The present times may not be

rather so propitious to either of them but in their close co-operation lies the bright future of both of them in the service of the country at large. Oil is an article of every day use, consumed by every strata of the society. With the increasing pace of industrialisation in the country and the subsequent raising of standard of living, the oil trade should carve out a bright future for itself.

While recapitulating, the following would in brief be the basic requirements for sustained progress and steady development of trading in vegetable oils on sound basis in the country :—

- (a) Standardisation of contracts having universal application;
- (b) Uniformity of rules and regulations, trade practices and weights;
- (c) Well organised and healthy forward markets in principal centres of trade;
- (d) Provision of cheap and durable containers ensuring elimination of leakage; provision of more tank wagons;
- (e) Centralised publication catering to the requirements of oil trade and industry for dissemination of market news of inter-state character;
- (f) exports of oils to foreign countries should be allowed to be made only subject to the terms and conditions of Indian contracts.
- (g) provision of oil storage tanks at principal centres of oil production and consuming centres and terminal markets by railway administration for internal trade and by Port Trust for export trade;
- (h) provision of tanker facilities in steamers for exports of oils in bulk.

Since the Oilseeds Crushing Industry is now considered a major industry by the eminent authority as Dr. Bhatnagar, the future of the vegetable oil trade is assuredly bright and it is earnestly hoped the trading community will rise from its long slumber and will take their proper place in the world trade in vegetable oils.

DISCUSSION

Dr. M. B. Ichhapuria informed that the foreign firms had been insisting on the uniform standard of oils much earlier than the Government came in the scene and that might not be taken as dictation.

Mr. Vishram replied that the standard of groundnut oil as required in Bombay by foreign owned firms was based on 1 per cent free fatty acids while in Madras and Hyderabad which supply the bulk of this oil, the contract terms was 3 per cent free fatty acids. So he could find no way of supplying a quality which never existed. In Calcutta also the contract term was 3 to 5 per cent free fatty acids.

THE REFINING OF VEGETABLE OILS WITH SPECIAL REFERENCE TO GROUNDNUT OIL

BY

KRISHNA GOPAL MATHUR,

Chief Chemist, Kusum Products Ltd., Calcutta.

Refining of oils in general consists of degumming, alkali treatment or neutralising, water washing, bleaching and even steam deodorising the crude oils which become essential for making them useable as edible and at times as technical oils.

For the purpose of this short paper, I would confine myself to alkali refining of crude vegetable oils with special reference to groundnut oil for subsequent processing for *Vanaspati* or hydrogenated oils.

Although the reactions entering the process of alkali refining of oils are well understood and are almost the same irrespective of actual method followed, yet the actual practice varies with the experience of the chemist and it would not be wrong to say that to some extent the subject tends to pass on to the domain of fine art.

It is common knowledge that whenever a caustic lye is added to oil it forms soap and emulsion and the tendency of the lye is to react on the fatty acids in preference to neutral oil. While this is true it is hardly a sufficient explanation as numerous other reactions are taking place at the time due to minute traces of surface active agents and other impurities that are present in the oils.

Further, this common knowledge that fatty acids and lye produce soap becomes more complicated as this chemical reaction takes place with any lye. The chemical reaction would be the same for weak as for strong lyes, but the physical properties would be different and of the physical properties it is the surface tension that, to my mind, plays the greatest part.

As lye of proper strength is added to oil during refining, soap is formed which reduces the surface tension of the lye solution to nearly that of the oil and naturally a good emulsion is formed. If the lye that is used is very strong it would have a higher surface tension than a weaker lye would at the start and as the soap is formed it would not reduce the surface tension of the strong lye to as near that of the oil as the weaker one, so that we would not have as good an emulsion formed, if any, as with a weaker lye.

In the first stage of refining a good emulsion is desired and this is done by bringing surface tension between the liquids to a very low value and is achieved by mixing and agitation. As heat is of importance to speed of chemical reaction, an optimum temperature is required.

Lye solutions and many other like salt solutions etc. have a salting out action on soap particles of the emulsion, but as long as the lye is reacting on the fatty acids or oils this force is overcome by the force of the chemical reaction. However, when the chemical reaction slows down and the lye becomes spent this salting out force comes into play prominently and is perhaps all important. Soap particles in water are in a colloidal state and it is not a true solution, but in this case a mixture of two liquids, the more concentrated forming the cell walls somewhat similar to honeycomb and the weaker taking the place of the honey. However, these cells are not closed like honeycomb, but are more in the shape of a sponge. The salting out action consists in a contraction by thickening and shortening of these cell walls thus almost squeezing out the liquid from between the cell walls. The stronger the lye the greater this contraction up to a certain point. Thus the salting out operation after neutralisation consists in contraction of the soap stock particles which are dispersed throughout the whole mass like fine pieces of a sponge holding the lye and oil between the cells. This process makes compact cells of soap stock thereby expelling the occluded oil to a great extent.

It sometimes happens while neutralising oils with higher percentage of free fatty acids that at the salting out stage a part of the lye is also squeezed out of the stock along with the occluded oil if not enough of excess lye or very weak lye strength has been used. This is due to the remaining lye in stock becoming too weak to effect the contraction or break. Both heat and salt in concentrated solution help in contraction or effecting the break but they have their limitations. As the colouring matters and other impurities are also squeezed out with the lye in such cases so we observe that the colour has gone back to the body of the oil.

From our above study of the reactions during oil neutralisations and from my practical experience of this subject of over 12 years I state the following generalisations which can be of great practical value in actual practice :

(a) The strength of the lye should be carefully chosen. It is best to select weaker lyes for refining low free fatty acid oils and more concentrated lyes for oils with higher free fatty acid contents. The lye strength should be such and it should be added in such excess

that after all neutralisation of the free fatty acids in the remaining lye should be sufficiently strong to effect a good break without the addition of much heat and salt.

(b) The temperature of the oil at the time of lye addition is equally important and it is a good practice to use low concentration lyes at higher temperatures and vice versa.

(c) The mode and speed of stirring at the time of lye addition and subsequently are also great factors in the emulsification and salting out operations. It is good practice to put the stirring to slow speed just prior to and after addition of the lye. Mostly for treatment of low free fatty acid oils with weak lyes no stirring is recommended.

(d) It is doubtful that the lye which gives the best break and settle over gives the best emulsion and the refiner must thus choose the lye that gives best results which are obtained by using a lye strength which requires addition of heat to complete the break to some extent.

(e) Best colour reduction is generally effected by the use of above method i. e. using higher Beume alkalies at lower temperatures.

(f) The lye should be added in the shortest possible period of time (except in the case of cottonseed oil) and should be added in excess depending on the exact nature and the amount of colour and other impurities besides free fatty acids present in the oil and to what extent they need be removed in the process of refining. The mode of sprinkling in the lye should be such that it takes up least air to the main body of the oil and stirring should not be turbulent, or else the soap stock will have a tendency to float up at comparatively low temperatures. Some refiners even use a mixture of 10% salt solution with the lye for neutralisation. Some refiners use a little quantity of water in suspension in oil for better emulsion at high temperatures while using more concentrated lyes.

Losses in Alkali Refining:

Due to the nature of the refining method which has been explained to some extent no chemist has so far been able to remove the impurities of the oils without some loss of the neutral oil. Thus the losses can be catalogued as:

- (i) Those losses which are unavoidable such as due to the removal of free fatty acids, dirt and grit, mucilage, gums, resins and other unsaponifiable matters.
- (ii) Those losses which can be avoided. That is the losses in neutral oil.

The efficiency of the refiner, his method and the equipment that he uses lie in how much less neutral oil he loses in the process, through occlusion and entrainment.

The general loss determination is on the percentage of free fatty acids present in the oil, and the most reliable way of finding neutralising loss is to subtract the weight of the refined oil from the weight of the crude oil before neutralisation. The difference represents the total loss. This is usually expressed as the percentage of the crude. As already stated the total losses consist of the avoidable and the unavoidable losses. This process of loss determination by weighment is not always possible in actual practice and so the analysis of soap stock and its percentage to crude oil are generally determined and the losses calculated on this basis.

The soap stock obtained generally by us in our refinery weighs about 4-4.5 times the free fatty acids present in the oil and its average analysis is found to be:—

	Per cent.
Total fatty matter	50
Water	about 40
Combined alkali	4.00
Other impurities such as gums, phosphatides, salts and other impurities	6.00

Out of the 50% total fatty matter present in the soap stock it is our experience that about half is neutral oil. On this basis suppose we treat 100 tons of groundnut oil of say one per cent free fatty acid contents we would generally get about 4.5 tons of soap stock which will have 2.25 tons of neutral oil in suspension. Thus in this case:—

Unavoidable losses are	2.25%
Avoidable losses	2.25%
Total loss.	4.50%

Much work has been carried out by us to decrease our avoidable losses which are not always of the same order due to the complex nature of the oils treated and their various impurities yet with the best kettle practice these cannot be much reduced. Also it has been found that oils with low free fatty acids up to 1% F. F. A. yield higher avoidable losses while the losses are slightly reduced with oils upto 2.5% F. F. A. contents and above this limit the losses are again more.

Our other findings are that if the oils are gum conditioned or degummed the avoidable losses can be reduced to some extent. At times apparently clear oils do have albumins in solution due to the solubilisation of phosphatides caused by bad and prolonged storage of the seeds prior to crushing in humid climates and high temperatures. My experience is that even traces of these dissolved albumins increase the avoidable losses out of proportion to the free fatty acids present in the oil. In such cases it is best to remove these gums by addition of a little quantity of salt or soda silicate, or phosphoric acid or alum and steaming the oil with open steam resting the charge for an hour or two and removing the gums and emulsion from below. However, for avoiding excessive avoidable losses it is best to centrifuge the albumin, water and oil mixture so obtained to recover neutral oil. The recovery can be made with the help of dilute sulphuric acid but the oils recovered are of darker colour and have a very high free fatty acids contents. This process is called degumming while several patents have been taken on gum conditioning wherein the gums are brought to a state that they coagulate to some extent and lose their surface active properties to some extent and thus alkali refining can be carried out without much extra loss neutral oil, in the presence.

As some free alkali is left in the soap stock so the analysis of stock is at times erratic. In U. S. A. generally Wesson loss is determined which accounts for free fatty acids, gums, moisture, gritty matter and unsaponifiables and the avoidable losses calculated. This to my mind is a more accurate method but correct determination of Wesson loss requires a good deal of practice and purest chemicals.

Modern trends in the refining of oil :

This paper cannot be complete without mentioning the modern ways and equipment of oil refining whereby the avoidable losses of neutral oils can be minimised if not altogether eliminated.

Our usual kettle or batch system of neutralisation suffers from the following defects.

1. Long time of contact between the oil and alkali resulting in higher degree of saponification of neutral oil.

2. Inefficient gravity separation of neutral oil in the soap stock.

3. Excess of alkali required to be added to get a good break attacks the neutral oil and is lost as edible product.

4. As the gravity separation of soap stock from the body of the oil is not complete some neutral oil is lost during subsequent washes in the form of emulsion.

Most of the above defects are more or less removed with the present day technique and modern continuous refining processes and some American makers of such plants sell them on 20-30% less loss of neutral oil basis as compared to the best kettle practice.

The advantages of the modern continuous centrifugal refineries are: (1) Not much excess of caustic lye is required as high speed of the neutralisation centrifuge not only controls and shortens the contact with alkali but can effect the break of much smaller particles of soap and so that the same degree of contraction is not required as is required for a kettle charge settling and break. This naturally causes saving in neutral oil (2) Methods have been developed in which a weaker saponifying agent like sodium carbonate which does not attack the neutral oil but reacts only with the free fatty acids of the oil even if added in excess can be used. Although sodium carbonate has the above advantage and is also cheaper than commercial caustic soda yet it cannot be used in the kettle practice of neutralisation as it gives out carbon dioxide during reaction with fatty acids of the oil which tend to float the soap, the soap stock is of such a nature that its settling time is very great, and that it does not attack the other impurities of the oil such as colour and other unsaponifiable matter thus the oil so refined has a darker colour and more impurities. However, this famous Clayton Process of Oil Refining by Continuous Centrifugal plant is rather difficult to operate and generally for oils like cottonseed even not recommended. (3) Prompt centrifugal separation of the soap stock from neutral oil leaving a minimum amount of free oil. (4) Less losses in oil are also claimed during washing of neutralised oils in specially designed centrifuges. Besides these centrifuges can be adopted for de-oiling the soap stocks from kettle refining although the neutral oil so obtained is of a little darker colour.

Very few if any refinery in India is equipped with the Modern Centrifugal plant although there is a definite advantage in following this method of refining by way of saving in neutral oil and workability of difficult oils like cottonseed. As the Government does not allow such plants to be imported, this restriction must be removed if the cause of more and cheaper edible fat availability for the masses of India is dear to the Government. Besides saving in neutral oil the refining costs are cut down by way of less labour and less electrical consumption by the use of Continuous Caustic Refining Processes.

RATIONAL UTILIZATION OF OIL-SEED WEALTH OF THE COUNTRY

BY

D. K. GUPTA,

Akhil Bharat Sarva Seva Sangh, Wardha.

Out of 24.7 crore acres of land under our principal crops, 2.6 crore acres are under oil-seeds. This 10.5 per cent of the cultivable land of our country is yielding 50 lakh tons of oil seeds annually. Out of this oil-seed produced, 39 lakh tons are available to fulfil our requirements of fats and oils. I want to place for your consideration, the fact that all these oil-seeds produced are primarily required for food. With the best of methods, we are not able to provide even an ounce of oil per *capita per diem* to more than 55 per cent of the people. That is the position in the country, which is one of the best producers of oil-seeds in the world. So the problem in a nutshell is, as we cannot increase the acreage under oilseeds due to scarcity of cereals, (a more primary requirement than oil), we have to rely on the 39 lakh tons of oil-seeds available for pressing and get the most out of it.

Let us look into the wastages that are involved in the present methods of production:

1. Large percentage of the oil is used in industries other than food. In a country, where we do not have oil enough even for our food needs, it would be wiser to make use of only non-edible oils for requirements other than dietary.

2. We are removing about 60 per cent of oil seeds from the producing areas and concentrating them to a small number of big cities and thereby incurring transport and storage losses in the oil-seeds. Certain oil-seeds are kept as kernels for facilitation in storage and pressing and in their case deterioration is still more rapid. Centralised storage in large amounts gives rise to conditions which spoils stored seeds and also leads to losses due to insects and rodents which make a regular home in the vicinity of the godowns used for the purpose year after year. In ports, where oil-seeds are collected in plenty, the humidity factor accelerates deterioration. So, we find that by allowing our oil-seeds to be pressed through centralised methods of production, we are allowing waste, which can be very well stopped if the means of production were decentralised in raw material producing areas.

3. When we look to oil as an article of food the cleanliness of oil and its nutritive value becomes a primary concern. We find that in mills, where hot process of pressing is resorted to, the oil obtained is dietetically inferior in quality and the initial acidity of the oil a little more than in that obtained by the cold press process. As the oil in a centralised mill takes time ranging from 2 to 6 months to reach the consumer in the 'muffasils', the free fatty acids are released in the oil to an appreciable quantity. These free fatty acids are dietetically useless and to that extent a waste.

4. Oilcake which is an important residue from the oilseed after the oil has been obtained, has a very high nutritive value and I do not think that we can continue to ignore its importance as a food for human consumption. All over the world in general and in India in particular, we will have to make use of the oil cakes for human consumption and that incidentally seems to be the only way to release some of the land from cereals, get it under oilseeds and thus increase the production of oils and fats. These oilcakes, if they are to be used for edible purposes, are to be very pure indeed, will mean that the oilseeds before pressing should be thoroughly cleaned and this is not possible in the large scale production in the oil mills. The oil seeds will have to be thoroughly cleaned before being pressed and that is possible only if they are pressed in small decentralised units. Moreover, where cleanliness can be more thoroughly done, the oilcake is a product which gets deteriorated very soon, its keeping quality being very low. Hence, the consumer must be provided with this product without any loss of time after it is once produced. Just now we are making little use of these 20 lakhs tons of deoiled edible oilseeds with high nutritive value and they are being lost as human food at a time when our country is compelled to import 60 lakh tons of cereals for our food.

The four points that are enumerated above lead to the conclusion that decentralisation in this important food industry is essential if we have to utilise our oil-seed wealth rationally. By decentralisation, the need for transport of oil-seeds to a central place through various collecting centres, will be eliminated. It will provide with a better quality oil in a fresher form and the oilcake thus obtained may be made use of for human consumption. In our country 37 per cent of the population lives in the villages which are both the producer of oilseeds and also its major consumers. Decentralisation will mean that we have to provide the raw material producers with certain means of processing, which will be befitting the village environments and work by making use of such motive power as are universally available there. For the last 15 years the village oil industry has been

an important subject of study and research with the All India Village Industries Association which I have the honour to represent, and we find that the bullock driven oil press existing in the village to-day, has great potentialities of improvement. It can serve as a model of a decentralised unit of oil-pressing. But at this stage a question may be asked that out of the 39 lakh tons of oils seeds available, these *ghanies* could not possibly give the same amount of oil as the nation can get with the help of centralised mills. I completely agree with it. But I submit that the improved type of village oil press can press out oil to the extent of only 2 to 3 per cent less than what can be got through centralised mills and I will place before you the figures to prove that in aggregate, the slow tortoise of the *ghani* wins the race over the mills. In aggregate, we find the total quantity of oils pressed by mills from the oilseeds procured by them is less in percentage than what we get from the same quantity of oilseed at our experimental station at Wardha. We find that except in the case of linseed, in all other oilseeds, the aggregate percentage of oil obtained by the Wardha *Ghani* was greater than the average percentage what the oil mills of India obtained, (Tables I & II). In sesamum the average percentage of extraction in the mills is 33.3, while in *ghani* of the improved type, it came to 44.5. In coconut the mills pressed 55.3 per cent, while the *ghani* got 59.5; with groundnut mills got 40 per cent while *ghanies* 43.1; while in castor and mustard, the percentage of oil is about the same. These figures about the mills have been taken from the statistics collected by the Indian Central Oilseeds Committee under the industrial Statistical Act, 1942, and the quantities of oilseeds crushed by the power driven mills coming under the operation of the Indian Factories Act, and according to the information received from 90 per cent of the mills in 1946. The figures for *ghani* are from Maganwadi, Wardha, from one year's production figures and the average taken for more than 1,000 charges of 9 seers each in the case of every oilseeds. In the case of linseed, oil mills express 33 per cent of oil and the *ghanies* 31.3. In aggregate, however, the *ghani* could have pressed more oil out of the seeds of India than what the mills have produced. This is due to the fact that there are certain losses in storage, cleaning and refining of the oil, which are more in the case of mills than in decentralised units of bullock oil presses, where the handling is better manned.

I will plead before you that, with the above facts in view, the bullock driven oil press is the answer to right utilisation of the oilseed wealth of the country. Apart from this, in a country whose population lives in villages, it will afford an opportunity of employment in the largely unemployed rural areas and to this extent

lighten the burden on the soil. It will give prosperity to the oil-seed producing areas and thus give an impetus for better production. It will make use of the existing motive power of the country without any extra expenditure. This, along with the excess and better food that the *ghani* will provide, should make us think in a direction of limiting the oil pressing in the mills to non - edible oil-seeds only or such oilseeds like cotton seed, which cannot be pressed in de-centralised units. The circumstances of to-day will force us to do that. I believe that the scientists will look at this problem in a dispassionate way and by a logical reasoning come to the conclusion that the best utilisation of a raw material for food is made only when it is processed and given to the consumer in the freshest possible state. This, when applied to oil-seeds, which I hold are primarily an article of food brings us face to face with *ghani*. I hope the scientists will be able to give more of their energies and talents in improving this decentralised method of production.

*TABLE I.

Oil obtained for groundnut kernel by mills.

Year	Wt. of kernels	Wt. of oil obtained.	% of oil.	% of oil average	Average in <i>ghani</i> %
1936-37 to					
1938-39	840	336	40.00		
1939-40	1051	420	39.96		
1940-41	1629	652	40.02		
1941-42	956	382	39.95		
1942-43	1259	504	40.03		
1943-44	1768	707	39.08	39.947	43.1
1944-45	1790	716	40.00		
1945-46	1608	693	39.98		
1946-47	1901	760	39.98		
1947-48	1736	694	39.97		
1948-49	1696	638	40.45		

* According to table No. 49 of the Indian Oilseeds Statistics 1948-49 figures, out of 15,96,000 tons of groundnut, 6,38,000 tons of oil is obtained.

TABLE II.

Comparative figures of oilseed crushed in mills, and aggregate percentage obtained and that of Wardha ghannies.

No.	Name of oil seed.	Seeds crushed in mills. tons	Oil got by mills tons.	% of extraction. yield.	Extraction in ghani % yield.
1.	Cotton seed	1,089	144	13.3	—
2.	Linseed	82,226	27201	33.0	31.3
3.	Rape	1,65,445	33646	33.0	33.0
4.	Sesamum.	6,284	2120	33.73	44.5
5.	Castor.	43,152	15972	37.0	37.4
6.	Coconut.	10,488	5806	55.36	59.5
7.	—	14,729	5126	34.83	33.6

DISCUSSION

Mr. V. D. Mariwala, Vice-President, The Oil Merchants Chamber and **Dr. M. B. Ichhapuria** of the Tata Oil Mills pointed out that the figures of 55.36 per cent for coconut oil from copra obtained by expeller as given by Mr. Gupta was very low. It always ranged from 63-64 per cent.

Mr. Gupta informed that the figures were based on the copra received and the oil extracted out in the mills. The *ghannies* figures were those that they obtained at Wardha. He was of the opinion that if *ghannies* were situated near the copra producing centres, much better yields of oil would be obtained because the copra that they received at Wardha was not of good quality.

Mr. Om Prakash, Oil Expert to U. P. Govt. pointed out the snag in Mr. Gupta's figures of the low yield of oil in mills. The reason was that the yield of the oil had been calculated on the total seeds received by the factory without taking into consideration that a part of the seeds were lost in transit and storage. He further differed with the views of Mr. Gupta that oil should only be extracted at the places where the seeds were produced in decentralised units. It was not practicable because each area was not self sufficient and there would be some surplus areas also. It was necessary, therefore, to transport the extra amount of seeds from the overproducing areas to centralised units so that the oil and the cake might be sent to those places where they were more required.

Dr. J. G. Kane of the Bombay University while disagreeing with the figures of oil obtained by expellers as given by Mr. Gupta maintained that a great wastage of oil seeds had been going on. It

was also not possible in many cases to extract whole of the oil by decentralised units. He was, therefore, of the opinion that the combination of centralised and decentralised industry as existed at that time in India was the best. A better method of packing of the seeds for transit and building better godowns were necessary to reduce their wastage. He further suggested that the cultivators should produce only the best quality of seeds in which they should be advised by their respective State agriculture departments.

Dr. J. S. Aggarwal (N. C. L.) agreed with the views of Dr. Kane and suggested that the village industries associations, who come more in contact with farmers, should impress upon them to grow only the best varieties of seeds. By this method they would render a great help to the country. Further a cooperative effort by villages and cities is necessary for the industrialisation of the country.

Mr. T. V. Subba Rao, of the Tata Oil Mills also agreed with the views of Dr. Kane and said that the oil crushing industry as existed then in India viz. by *ghannies* in villages and big mills in cities was quite satisfactory leading to an even distribution of oil and the cake.

Mr. Gupta, while agreeing on some of the points put forward by the previous speakers was still of the opinion that only that amount of the seed might be taken to big crushing mills which were in excess and not required by the villagers. By this plan the poor cultivators would not be deprived of their produce and thus they would be saved from starvation.

OIL
EXTRACTION

NUTAN-GHANI

BOMBAY STATE GOVERNMENT'S IMPROVED VILLAGE OIL *Ghani*,
DRIVEN BY A BULLOCK

BY

G. V. DATAR

Village Industries Experimental Workshop, Poona.

The Department of Industries, Government of Bombay conducted the experiments under the supervision and guidance of Mr. Haskell, the then Industrial Engineer, since the year 1939 and constructed improved type of *Kolhu ghani* for introduction in the Province as *Haskell Ghani* in the year 1941.

Further experiments were carried out at village industries experimental workshop, Poona, in the year 1948 and a design having less complicated and less costly parts but having the same efficiency as that of *Haskell Ghani*, was constructed and is now put forth as *Nutan Ghani*.

Haskell Ghani or *Nutan Ghani* is a bullock driven *Kolhu Ghani* having a wooden mortar and a pestle, but is fitted with mild steel weight beam and ball bearings, instead of wooden weight beam and wooden bearing or *Makadi*.

By introduction of ball bearings, the friction is reduced and thereby, draught is also reduced and thus the bullock get less fatigued.

The weight beam instead of sliding on the mortar side is entirely suspended on the pestle top, which exerts more pressure on the seeds compared to that of sliding type of weight beam and thus it helps to get quicker extraction.

The weight beam of *Kolhu ghani* is not designed after considering the convenience of the bullock, but is normally designed in such a way so as to accomodate the *ghani* in a restricted space. Normally, the *ghani* is installed in an area of 12' x 12' and hence the bullock has to move round the *ghani* by bending its back on one side, which results to develop a permanent deformity in the back of the bullock.

The weight beam of the improved *ghani* is designed with a view to get the maximum possible advantage of leverage and to give free movement to the bullock so that any physical deformity may not be

developed. This *ghani*, therefore, necessarily requires 15' x 15' area without any post as pillar of support coming in. The equipment consists of following parts:—

- (1) The weight beam of mild steel angles and flats fitted with two rollers having two ball bearings;
- (2) One wooden pestle fitted with mild steel forged cap and cast iron housing with one ball bearing and one mild steel band ;
- (3) Yoke accessories consisting of one ring, two pins, one bolt and one hook.

The cost of equipment is Rs. 265/- approximately.

The equipment can be accomodated in the *kolhu ghani* mortars if available with the *telis* or mortars can be prepared out of a log of wood of 39" dia. and 4 to 5 feet length of *babul*, *tamarind*, *neem*, *siras* or *phanas*.

If wooden logs are not available, R.C.C. mortar can be constructed at the estimated cost of Rs. 150/-.

Mortar pit consists of two parts (1) pit lining or *pacher* and (2) pit bottom.

- (1) Pit lining or *pacher*, the replaceable parts, are required to be fitted to mortars irrespective of mortar material (Wooden or R.C.C. mortars). These *pachers* are prepared out of four *babul* wood pieces of 12" dia. and 18" length.
- (2) The pit bottom which need not to be replaced often, is to be prepared out of *babul* wood piece of 13" dia. and 6" length and is fitted in the mortar pit.

These parts-lining or *pacher* and pit bottom, can be prepared and fitted by the local carpenters according to the dimensions.

The pestles can be prepared out of log having 30" to 36" midgirth and 4'-6" length. The best wood for pestles is *babul* wood, but *kusum*, *Anjan*, or *Khair* also can be used if *babul* is not available.

Working capacity of improved *ghani*:

With this improved equipment by using only one bullock in a working day of 8 hours and one hour's total rest in three instalments given to a bullock, the seeds generally in use can be pressed as mentioned below (Table I).

TABLE I

Seeds pressed	Q'ty p. day lbs.	No. of char- ges p. day.	Oil extracted p. day, lbs.	Cake available per day. lbs.	per cent extra- ction.
1 Ground nut...	200	10	70 to 86	128 to 114	34-43
2 White til ...	200	10	80 to 90	120 to 110	40-45
3 Coconut ...	300	15	165 to 180	135 to 120	55-60
4 Niger ...	200	10	56 to 60	144 to 140	28-30
5 Safflower decorticated...	300	15	144 to 150	156 to 150	48-50

To get the above results, the bullock must have its own weight of 800 lbs. and it must move round the *ghani* with a speed of 250 to 300 rounds in 45 to 50 minutes. The total weight of 448 lbs. will have to be placed on the weight beam.

From the above table, it will be seen that the working capacity of this equipment is more than double than that of any country *ghani* at present in use in our province. Similarly, there is a gain of two to three per cent of oil due to the arrangement of bringing the weight beam on the pestle head and there by increasing the intensity of pressure on the oilseeds.

The percentage of oil extraction depends much upon the total oil contents of the seeds.

With a view to introducing more efficient equipment compared with that of country *ghani*, Government sanctioned a scheme namely the "Village Oil Industry Scheme" which functions under the Joint Registrar for Industrial Co-operatives and Village Industries, Poona, Co-operative Department, Government of Bombay. The equipment is given to *telis* and their societies on loan *cum* subsidy basis.

THE FUTURE COTTONSEED OIL MILLING AND ITS UTILIZATION IN INDIA.

BY

DR. K. S. MURTI,

Oil Technological Institute, Anantapur (Madras)

India is probably the oldest cotton producing country in the world. As for production of cottonseed in India, it is a matter of common knowledge that it ranks second in the world, next only to U.S.A., with an average annual production of about 2,000,000 tons before partition. However, this position has somewhat altered since the partition of the country and India occupies at present probably the fourth place, next to U.S.A., Russia and possibly China. Based on the statistics furnished by the Directorate of Economics and Statistics, Ministry of Food and Agriculture for production of cotton in India during the last three years, it is estimated (using an average ginning factor of 30) that the total production of cottonseed in India after partition for the last three years is as follows:

TABLE I

Year	Production of cottonseed tons
1948-49	9,02,000
1949-50	10,95,000
1950-51	12,20,000

The more important cotton producing States in India in the decreasing order of importance are Bombay, Madras, Madhya Pradesh, Hyderabad, Madhya Bharat and Sourashtra.

According to the Five Year Plan, it is proposed to realise a production of 4,000,000 bales (of 400 lbs. each) of cotton in India for the year 1951-52 and to further increase it progressively to 5,200,000 bales by the year 1955-56². This means a production of 1,667,000 tons of cottonseed during 1951-52 increasing to 2,250,000 tons by 1955-56, which will be maintained thereafter. When this is achieved India's position in the world production of cottonseed will be second as before partition.

While it will be noted from the foregoing, that though India is the oldest cotton producing country and the second leading cottonseed producing in the world, it is regrettable also to note that it is the last in the matter of industrially utilising the seed to obtain the much valued products, particularly the oil and the cake.

The Economic Significance of Cottonseed Milling Industry to India:

When cottonseed is processed, the products obtained are the oil, cake, linters and hulls. Assuming that ultimately 75% of the seed produced in India is processed (in U.S.A. about 86% of the seed is processed) and on the basis of an average yield of 15 per cent oil, 45 per cent cake, 4.5 per cent linters, 25 per cent of hulls and the rest trash, dirt and processing losses, roughly 1,87,000 tons of oil, 5,63,000 tons of cake, 60,000 tons of linters, and 3,15,000 tons of hulls can be produced from 1951-52 production of cottonseed. When the Five Year Plan has been materialised, the corresponding figures will be roughly 2,53,000 tons of oil, 760,000 tons of cake, 84,000 tons of linters and 422,000 tons of hulls. Estimating on the basis of the crude oil price @ Rs. 1600 per ton, i. e. Rs. 100 less than the price for crude groundnut oil per ton, this means a production of crude cottonseed oil of the value of about 30 and 38.5 crores of rupees respectively now and after 5 years. If to this is added the value of the other products namely, the cake, linters and hulls and their utilisation it will be seen that the economic possibilities are tremendous to the country by undertaking processing of cottonseed for oil and other products³.

The present poor condition of the industry in India and the factors contributing to it:

It is stated ^{4,5} that before partition 15 per cent of the cottonseed produced i.e. 300,000 tons was being utilised for the production of the oil annually. This estimate should be taken with reserve, as it is understood that there are at the best 3 or 4 mills processing the seed intermitantly on modern or semi-modern lines. The maximum installed capacity of these 3 or 4 mills together will account only for about 27,000 tons annually. There seem to be about a dozen other small mills mostly in Madhya Pradesh, crushing at the most about an other 20,000 to 22,000 tons of the seed bringing the total to about 50,000 tons at the most, producing annually not more than 7,000 tons of oil. This works out roughly to 5 per cent on the total seed produced in the country at present.

The present processing practice of cottonseed in India seems to be of two kinds. According to one practice, the seed is cleaned, delinted and dehulled, and cooked and the oil is obtained from the meal by hydraulic presses or expellers and then refined. According to the second practice the seed is not properly prepared at all but pressed whole without removing the lint or separating the hulls. Consequently, the oil so prepared is less in yield, much darker in colour and presents great trouble in refining which could not always be done successfully and the soap stock is too dark in colour to be used in soap plants. On account of these troubles, one of the well known establishments in Bombay State has tried and given up processing of cottonseed. Thus the imperfect processing procedure, obviously carried with equally imperfect technical knowledge of processing only helps in retarding the establishment of the industry.

The reasons responsible for the cottonseed processing industry not taking any root in India are several. First and foremost of these is the prejudice of the farmer against feeding the cattle with the pressed cottonseed cake, presumably based on his misapprehension that the cake without the oil is not a good feed. The conservatism of the Indian farmer acts as a powerful deterrent from his trying any change even after it is explained to him that the cake is a better feed than the whole seed. A second factor, perhaps even more important than the first, is the lack of full knowledge of the technique of the cottonseed processing and information of the composition and uses of the various products obtained. Thirdly, unlike most other edible oils like groundnut, coconut, sesame or mustard oil available in India, crude cottonseed oil cannot be used for edible purposes directly without refining. These coupled with the difficulties met in refining crude cottonseed oil as at present produced in India, appear at first sight to present a great impediment in undertaking the cottonseed processing. Fourthly, in the absence in India of the existence of chemical industries absorbing raw materials like the linters and the hulls and the lack of full knowledge of the uses to which these can be put, the processor is compelled to export the linters to foreign countries for disposal which is uneconomical, as he is to compete with linters produced in the importing countries like U.S.A. This operates against economic disposal of some of the products. Fifthly, the quality of the oil produced by the current practice is too dark in colour with high free fatty acid content. The soap stock produced in refining such an oil is so dark that it finds no outlet, not even in washing soap industry. Sixthly, the yield of oil is low, due to inefficient processing procedure adopted. The average oil content of the Indian seed is about the same as that of the cottonseed in U.S.A. But due to imper-

fect processing the average yield realised in the mills with expellers or hydraulic presses is 12-13 per cent (and in some cases a maximum of 14 per cent) as against 15.5% oil realised in U.S.A. This low yield of oil realised makes all the difference in the working of the milling operations economical. In this connection, the very high and speculative prices of cottonseed prevalent in the Indian market and the relative non-availability of the seed for processing are also operating at the present time against the spread of the milling industry.

Lastly, the present nonversatility of the oil mills makes them useful for processing only one kind of oilseed. Single purpose oil mills are placed in an unfavourable profit position by unfavourable finished product or raw material prices causing to endure daily operational losses. To shut down a mill under such conditions entails an even greater financial loss. This problem will be greatly alleviated by installing a multipurpose plant i.e. by equipping mills to handle several oilseeds. In that case, it can stop processing any particular oil bearing material when market conditions become unfavourable and start processing another oleagenous material where prices are satisfactory. Again, a versatile oil mill overcomes a heretofore serious defect in oil milling practices. The extraction of cottonseed (or any one vegetable oil usually) is highly seasonal, resulting in the mill being idle during a part of the year. But if the mill is equipped to treat more than one oil seed, it can switch over to another oil bearing material thus ensuing continual profitable year.

Modern cottonseed processing technique :

Having stated the present backward condition of cottonseed processing in India, it may not be out of place to give a brief description of the latest cottonseed processing technique as prevalent in U.S.A. which is the biggest cottonseed producing and processing country in the world. Cottonseed are unloaded and stored in huge seed houses sufficient to process for the whole year or as long as possible. The seed houses are specially designed to ensure constant suction of air through the seed, thus cooling it to prevent its heating up which may result even in burning up of the seed sometimes. The seed from the seed house are then run through sand and boll reels to remove the foreign matter. The seed brought to huge work bins are given a second cleaning with pneumatic type cleaners to remove any sticks, bolls, stones, sand, etc. that the reels did not remove. The next operation is the removal of most of the lint from these cleaned seed, either in one stage called "mill runs" or in two stages called first and second cut linters by passing the seed through delinting

machines. This lint is cleaned and baled. The delinted seed are then dehulled in the hullers where the seed, are cut up to allow the hulls to be separated from the meats by shakers with air nozzles attached to the end of the tray. The separated hulls are then beaten to remove any fine meats that might be clinging to them. The separated meats go over a purifier-shaker where only enough hulls are removed with air nozzles to control the protein in the finished meal (cake). This is one of the difficult and most critical operations in the processing of cottonseed requiring skill and experience. The resultant meats are passed over horizontal flaking rolls. The flaking operation is necessary in order to reduce the meats to a thickness between 0.005 and 0.010 inches which facilitates in the oil cells being easily disrupted in the succeeding operations yielding oil more readily and to a greater extent. The next operation is cooking or tempering the meats which is usually done in a stack cooker. This is necessary whether for hydraulic or screw press extraction in order (1) to rupture or finish the rupturing oil cells, (2) to increase the fluidity of the oil, (3) to precipitate phosphatide material in order to produce oil of lower refining loss, (4) to facilitate separation of oil from other materials in the seed, (5) to detoxify free gossypol and (6) to destroy moulds and bacteria. Cooking is also done in the cookers fixed on the top of the more modern expellers themselves. If expellers are used instead of hydraulic presses, the oil flows into a screening tank where most of the foots are removed continuously and returned with the feed to the expellers. A part of the oil is pumped to filter press and thence to storage and another portion directly sprayed over the barrels of the expellers to cool them. It is important that some means of temperature control be provided for screw press barrels either by providing water or oil cooling. This improves the oil colour and quality, gives lighter coloured cake with lower oil content. The oil thus prepared in expellers or hydraulic presses is light coloured, easily refined and bleached.

The use of screw press (expeller) method of extracting oil from cottonseed has increased considerably in the United States recently. Under proper operating conditions the oil left in the cake is less than in the cake produced by the conventional hydraulic method. Another definite advantage of the expeller method is its low labour costs compared to hydraulic press though this is to some extent offset by higher operational costs.

Next stage in the development of the cottonseed milling industry in U. S. A. is the introduction of continuous solvent extraction. After preparing the seed as for the screw pressing process upto the stage of flaking and even cooking, the meats are extracted by

solvent. Several systems of continuous solvent extractions have been developed and employed. The most common solvent used is commercial hexane. However, even the best and most efficiently operated plant could not reduce the extraction to less than 2 per cent on the average where as in the case of solvent extraction of soyabean, the extraction could be reduced to 0.5 per cent oil in the residual cake.

The latest development in the cottonseed milling in the States is the combination of pressing by expellers and solvent extraction. Cottonseed meats after separation of the hulls contain about 30 per cent oil in them. After the usual treatment, these are prepressed in an expeller to leave an oil content of about 12 per cent in the cake which is then conveyed to the flaking rolls. The flakes from these rolls are then conveyed to the top of the extractor in the solvent plant.

Refining of Crude Cottonseed Oil:

Provided the processing of the cotton seed is followed properly as described above, the refining of cottonseed oil will not offer any insuperable difficulties, although the crude oil will always be darker than crude groundnut oil. The conventional kettle method of refining consists of the same procedure as for groundnut oil, with some suitable modifications, details of which can be had by a reference to "Cottonseed and cottonseed Products" by A. E. Bailey. In addition to the conventional kettle refining, continuous caustic soda method and continuous soda ash-caustic soda methods have come into vogue since early nineteen thirties and these processes are extensively employed in the U.S.A. The advantages of these continuous methods over the kettle process are decisive, firstly, because there will be a net saving for prime crude oil by the continuous methods of 1.5 to 3.0 per cent over the open kettle, i. e., the saving in the loss of neutral oil will be 25 to 40 per cent of the losses in the kettle method. Secondly the continuous processes are not nearly so dependent on the judgment and experience of the refiner as is the case with the open kettle. The adoption of the continuous refining process (employing either sharples or de Laval's centrifugal equipment) has been almost universal in the refineries in the United States.

Steps necessary to be taken to establish the Industry on proper lines:

It is essential to create the necessary atmosphere for the establishment of the industry on proper lines. This can be done firstly by educating the farmer about the wastefulness of feeding the cattle with the whole seed instead of the more nutritious and wholesome cotton cake. Careful experiments have shown that animals can grow on

rations containing very small amounts of fat but which supply sufficient amounts of protein, minerals, vitamins and carbohydrates. Further recent investigations of Burr and others have shown that for the growth of animals small amounts of certain unsaturated fatty acids are essential and must be present in food or the animals fail to grow⁶. The amount of oil left in the cake by the best methods of screw pressing is found adequate to meet this nutritional requirement. On the other hand, the much higher digestive protein content of the decorticated cottonseed cake (34-38%) as compared to 17% in the whole cottonseed is a definite advantage to the animal, if fed on the cake. Moreover, the fuz present on the whole seed is fibrous and rather hard to digest. It is mostly removed during cottonseed milling.

Oklahoma Extension Bulletin 321 says "cottonseed contains slightly more than twice as much crude fibre as cottonseed meal and about twice as much oil as the meal (seed often contains 3 times as much, or more oil), choice cottonseed meal contains almost 3 times as much digestible proteins as the seed. A large amount of oil in cottonseed is not only an uneconomical feed, but it is likely to cause cows to go "off feed" and cream obtained from cows fed cottonseed churns into a hard, tallowy butter".

From feeding experiments conducted as early as 1914 in the Government Military, Diary Bangalore, its Manager Mr. S. W. Rouse stated "there is no better feed as a concentrated ration for milch stock than cottonseed meal. The animals take to it greedily, and will consume from the first as much as is put in front of them. Animals thrive and do better on it than on any other rations⁷⁻⁸". From the foregoing clear evidence of the superiority of cottonseed cake as a better feed than the whole cottonseed, it should not be difficult to educate the farmer about it.

In the meanwhile, it is considered very desirable in the interests of the cattle itself and to prevent the wastage of the valuable linters at this period of cotton shortage in the country that there should be promulgated some sort of a regulation that cottonseed should not be used as animal feed unless the fuz is mostly removed, i.e. only delinted cottonseed should be used for the feed.

Technical data on the Indian cottonseed must be made available.

Most of the other reasons stated earlier as responsible for the industry not taking proper roots in the country are due to the lack of full knowledge of the correct technique of cottonseed processing and full information regarding the composition and uses of the products, namely, the oil, cake, linters and the hulls. It is surprising to note the

paucity of such information in published literature. The only work is that of D.Y. Athawale published in the Indian Farming Journal 1944 giving analyses, besides other information, of about 88 samples of seed from different parts of India. Barring this, there are analyses of a few samples of cottonseed either published or in official records here and there. The only other published analysis of cottonseed, are in Indian Cottonseed Growing Review, 1948, and the report on the "Vegetable oil industry of Hyderabad state published by the Nizam's Industrial Trust Fund in 1930, both of which give analysis of a few samples of the seed. In addition to these, I could find the analysis of about 20 samples from South India in the record of the Government Agricultural Chemist, Coimbatore and from a few persons in touch with the industry by private correspondence. But what is required to stimulate the starting of the industry systematically and to thrive is not mere analysis of large number of samples but a complete technical data on the characteristics of the Indian cottonseed and their products. That is to say it is essential to study the composition of several varieties of Indian cottonseed, their variation with seasons and locality, with regards to proteins, oil, colouring matter, the gossypol, the lint content and its nature, the amount and composition of the hulls in the seed on a very extensive scale. Besides these, the behaviour of the Indian cotton seed on storage and the proper storage conditions thereof, require extensive study. With this object in view, the Government of Madras have already decided to conduct such investigations on pilot plant scale at the Oil Technological Institute, Anantapur. The subject is so vast and interests at stake are so high that it is quite essential that several research organisations should undertake this work simultaneously on a co-operative basis.

In this connection, I may state that in such an industrially advanced country as the United States, there are several research organisations in the several cotton producing states like Arkansas, Texas, Tennessee, South Carolina, Oklahoma, and Mississippi which are carrying on research on the various aspects of cottonseed industry and the United States Department of Agriculture are actively collaborating in this work. In addition to these the various machinery manufacturers and cottonseed processing firms carry out their own research on the several of these problems of cottonseed industry. No wonder then that the cottonseed industry is one of the most important oilseed industries in the States, giving a return of about 100 crores of rupees to the farmers annually for the production of cottonseed alone.

If there is need to carry out investigations on such an extensive scale in the United States, there is even much greater need to immediately undertake research both of the industrial and fundamental

type in India at various centres particularly in the major cotton producing states. It is further hoped that the Council of Scientific and Industrial Research and the Indian Central Oil Seeds Committee will take more interest and give a right lead and financial aid and coordinate the work in this field with no further loss of time. It is also to be hoped that the industrialists too will show more initiation and enterprise in the matter than hitherto and help in increasing the vast potential wealth of the country in this field.

APPENDIX

THE USES OF THE VARIOUS COTTONSEED PRODUCTS:

1. **Oil Edible:** as refined and deodorized oil for cooking, in shortenings, margarine, as salad oil and other products.
Non-edible : In soap, lubricants, sulphonated oil, pharmaceuticals, protective coatings, rubber, etc. Foots mostly in soap making.
2. **Cake :**
 - (1) Mainly as cattle feed in different sizes and forms.
 - (2) As a fertiliser (less than 10%). The cottonseed meal used as fertiliser is naturally of low quality and includes a certain amount of moldy or otherwise inedible meal.
 - (3) Other uses such as for technical protein; products and plastics are only in experimental stage.
3. **Linters:**
 - (1) *As fibre material:*
Long fibre linters as cotton felt for padding of mattresses, furniture and upholstery and other similar uses.

Purified and bleached cotton linters are used to some extent in paper making, as plastic fillers and artificial suede, and in the preparation of surgical dressings.
 - (2) Chemical uses: As a source of cellulose for chemical industry—in nitrocellulose industry and viscose rayon manufacture.
 - (3) For chemical cotton for Cord rayon, etc.

4. **Hulls :**
1. Largest use as a source of roughage in dairy; superior to certain hays and grasses.
 2. As a soil conditioner.
 3. In phenolic plastics as filler.
 4. As sweeping compounds.
 5. For production of furfural.
 6. Bedding material for road construction.

REFERENCES.

1. Dantawala M. L. "A hundred years of Indian Cotton" P. 1. East India Cotton Association Ltd., Bombay.
2. Presidential address by the Vice-President, Indian Council of Agricultural Research of the Sixty-fourth Meeting of the Indian Central Cotton Committee, Bombay on 27th July, 1951.
3. Utilisation of Indian Cottonseed, D. Y. Athawale, Indian Farming Journal, 1944,306.
4. Report on the Panel of Oils and Soaps Industries, Government of India, P. 12.
5. "Feeds and Feeding" by Morrision. P. 85.
6. *Journal of Biochemistry*, 1929, 345-367; 1930, 587-621; 1932, 1-19, etc. Tange Imp. Academy, Japan, Proc. 8 1932, 190-93.
7. Feeds and Feeding by Morrision p. 98, 366 and 982.
8. Cottonseed Products by Shri C. Ranganatha Rao Saheb, Mysore, published in 1914.

DISCUSSION

Dr. M. R. Mandlekar, Deputy Director, Industries, Bombay, informed that in connection with the cottonseed milling industry certain resolutions were passed by the Indian Central oil seeds Committee, as a result of which the Bombay Government appointed a committee to suggest whether any further research work on cotton seed milling was necessary. The Committee came to the conclusion that inspite of the information available, people had still prejudices that cotton seed cake would not be fit for cattle feed and therefore the point needed still further clarification. Another point was to find out the oil contents of various varieties of cotton seed available in that state particularly in Khandesh, Gujrat, Ahmedabad, Bijapur and Hubli. It was done and the oil contents in these varieties had been found to vary 12 to 18 per cent. It was further given out that a cotton seed expression plant was functioning in Nausari and two more were expected to come into operation shortly.

Dr. S. A. Saletore mentioned that the difference in prices of cotton seed and its oil was much more in India than in America. The lint contents of various varieties of cottonseed grown in Hyderabad state had been found to vary from 3 to 8 per cent. A factory at Hyderabad was working with great difficulty for the last six months as it was not able to sell the lint. He was of the opinion that the Government should start some plants for cottonseed milling and work out the cost of production of the oil. This would give inducement for the private enterprise in that direction. He agreed with Dr. Murthi that a great deal of research and development work on cottonseed milling was necessary.

Mr. Om Prakash felt that cottonseed cake would not fetch good price unless the superstition of feeding the whole cottonseed rather than the cake was removed from the people. In his opinion the solvent extraction of the cottonseed should be adopted in India in order that the cottonseed crushing might be economical.

Dr. Murthi replying to various speakers while welcoming the proposal of further work to establish the utility of cottonseed cake for feeding cattle, pointed out that they should gain experience from the information already available. It was simply a matter of habit that animals in U.S.A. would not take the whole cottonseeds just in India they might not eat the cake. The lint which is always there on the whole cottonseed would be harmful to the cattle. Moreover the cake would contain more proteins than the seed. He further informed that the analysis of 88 samples of cottonseed from various provinces gave the oil contents varying from 17.5 to 24 per cent in majority of cases. This amount of oil was net less than that present in American varieties where it varied from 18 to 20 per cent.

PROSPECTS OF OIL MILLING INDUSTRY IN INDIA

BY

VALLABHDAS V. MARIWALA, J. P.

Vice President, Oil Merchants' Chamber Ltd., Bombay.

In the growth of the Indian Society from earlier times, and subsequent economic and industrial development of the country, the oil crushing industry had not advanced farther than what an indigenous cottage industry would normally do. It functioned more or less as a rural *ghani* industry having local appeal and utility. Like the flour-milling industry, which having shed its phase as indigenous industry emerged and developed as an important industry in the present century, the oil crushing industry also has undergone the same line of progress and emerged as a major industry in the current century, from its confines of an indigenous cottage industry. An influential and larger section of India's mercantile and industrial community were not so much inclined to take to this industry and impart to it the benefits of their business acumen, experience and resources for its development. This has, however, been offset to a certain extent during last several years.

The policy adopted by the British regime was also greatly responsible for the lack of progress of this industry. The British had their own oil crushing industry in Great Britain fulfilling useful function on their economy. They were, therefore, mainly interested in Indian oilseeds as raw materials to feed their local crushing industry with a view to provide incentive to this industry and obtain valued stocks of oilcakes for manure and cattlefeed purposes in their country. They were solely guided by these considerations and were, therefore, averse to oil crushing industry developing in this country. The result was gradual increase in exports of oilseeds, which would be evident from the following figures:—

<i>Year.</i>	<i>Export of Oilseeds.</i>
1880—81	508,876 Tons.
1890—91	739,950 Tons.
1901—02	1,139,328 Tons.
Prewar average of the 1st World War i.e. before 1914.	1,443,000 Tons.
1st World War average 1914—18.	700,000 Tons.
Post 1st world war average	914,000 Tons.
1924—25 to 1936—37	1,344,800 Tons.

The crushing industry, therefore, received no fillip from the British regime in this country. Another substantial factor also needs mention. A good deal of our population used to cherish both liking and fancy for *ghani* oil in preference to power mill oil. This factor may also be to a certain extent considered as responsible for apathy towards oilcrushing industry. Extensively spread as it is all over the country, the crushing industry came to the fore mainly as a result of the impetus derived during the period of the last world war. Our export outlets to Germany and France, which were leading buyers of our oilseeds, were cut off for a considerable period during these years and hence exports of oilseeds dwindled accordingly. This contingency provided indirect impetus to the crushing industry to consolidate its position and advance its progress further. During the period of war, there was great demand for animal *ghee* by the army personnel but it was well-nigh impossible for the Government to cope up with such a voluminous demand. The British Government, therefore, encouraged setting up *Vanaspati* manufacturing companies in the country on an increasing scale and their number increased rapidly in various parts of the country by as much as five fold. This factor lent considerable momentum towards the development of oil crushing industry.

But unfortunately there was a snag in the rushing march of this industry, because it was devoid of rational approach, technical considerations and planned development programme in general. Consequently under the stress and strain of the changing times, the industry developed in a haphazard manner and very little attention was devoted towards technological, economic and other aspects of its working and future development on a long range basis. Herein lay the main weakness of this highly important industry. A valuable opportunity, was thus lost to fully avail of the advantages that would have otherwise followed from the course of proper planning and rational development, having due regard to the technological aspects of this industry.

The following facts should, however, inspire confidence amongst the oil milling industry for due to its inherent utility, it has been assigned to play a very important role in our national economy:--

- (a) In the context of present food shortage in the country, the edible oil constitute one of the chief sources of nourishment for the people as a whole. By increasing its production, the industry would be better serving the community at large in improving the standard of living.
- (b) The industry is spread all over the country and provides livelihood to lacs of employees which include technicians, skilled and unskilled workers, managerial staff, clerks etc.

According to third census of manufacturers (1948) there were 991 factories (oil mills) in the country, employing 58,164 workers with a total wage and salary bill amounting to nearly Rs. 3.37 crores and the capital invested being over Rs. 33 crores. These figures which have found an increase subsequently relate only to oil mills registered and working under the Factories Act but there are hundreds of unregistered oil mills in the country located in various parts. The total number of oil mills in the country including both registered as well as unregistered oil mills is estimated to be in the vicinity of 3000 having total annual crushing capacity of about 33 lac tons, with nearly 3600 expellers, 8500 rotories, 500 screw presses, 100 hydraulic presses and 15000 power crushers, etc. The industry is not in a position to fully utilise its total crushing capacity due to several factors. However, through its operations, it renders available to the country about 7 to 8 lacs tons of oilcakes, useful both as cattlefeed and manure, having an added importance in the present difficult time of food shortage in the country.

- (c) This industry also acts as a nursery providing raw materials in the form of oils to several important industries, viz. *Vanaspati* industry which is wholly dependent upon this industry for its supplies of raw materials, soap industry, paints and varnish industry, etc. Oil is also an important ingredient in the manufacture of lubricants, candles, oil cloth, etc.
- (d) The industry of manufacturing containers, viz. tins, barrels etc. derives great support from the oil milling industry, which also due to voluminous movements of oil in different parts of the country, yields considerable transport revenues to the railways.
- (e) The oil milling machinery and other spare parts manufacturing industry is vitally connected with the crushing industry.
- (f) Over and above these aspects of internal character, the crushing industry has another significance from the view of our export trade which has greatly benefitted thereby. In comparison with oilseeds, exports of oils would now loom large in our foreign trade. These commodities have been earning very valuable foreign exchange (worth crores

of rupees) for our national exchequer, as would be evident from the following figures:

<i>Export of vegetable oils in :</i>	<i>Value.</i>
1947—48	Rs. 11.49 crores.
1948—49	Rs. 10.85 crores.
1949—50	Rs. 8.79 crores.
1950—51	Rs. 21.44 crores.

Looking to the importance of crushing industry in the national economy of our country and the present state of affairs, which is far from satisfactory, as a number of oil mills in various parts of the country have been functioning as uneconomic units occasionally facing partial or complete closure due to various factors viz., oilcake procurement policies adopted by some State governments, shortage of raw materials, transport difficulties, technical shortcoming, etc. I would like to suggest the following remedial measures in this behalf:—

- (a) In order to achieve technical efficiency, higher type of oil milling and refining machinery should be manufactured in India, only such machinery as would ensure greater output of oil from seeds at less cost should be allowed to be installed in the oil mills and refineries ;
- (b) a country wide legislation should be enacted to see that the oil content in the cake should not exceed the necessary minimum percentage and further that only such cake should be marketed, The Government may even buy stocks of such oilcake at market price so that production of oilcake having greater percentage of oil content may be discouraged ;
- (c) Total ban over exports of oilseeds so that the crushing capacity may not have to remain idle ;
- (d) The Indian Central Oilseeds Committee, a body which should be mostly concerned with the progress and development of this industry, should organise and intensify its research activities, so that its research department can better serve the crushing industry as an advisory body ;
- (e) research for providing improved types of containers as would eliminate leakage of oil due to transit in transport movements ;
- (f) provision for erection of oil storage tanks of various sizes both at principal producing centres and consuming centres as well as terminal markets by railway administrations for internal trade and by port trusts for export trade.

D

providing tanker facilities in steamers for bulk movements of oils ;

- (g) provision of forward markets in oilseeds and oils at the earliest at principal centres of industry and trade on healthy lines ;
- (h) the Central Government should chalk out and implement their policy regarding export and import trade in vegetable oils in such a manner as would strengthen and facilitate the development of this industry ;
- (i) standardisation of contract, including inter alia F. F. A. terms for Reciprocal contract so that better quality oil may fetch some premium and derive encouragement for its production ;
- (j) centralised research and technological institutions for providing both teaching and training to oil technologists ; as well as facilitating research work in greater scale on allied industries viz. *Vanaspathi*, Soaps, Paints, Varnish, etc.
- (k) improved varieties of oilseeds having rich oil content.

Our country has to make many strides in the industrial sector of our economy. The oil crushing industry will have to play its own part in this task and it is high time that the industry puts its own house in order so that it can better equip and prepare itself to bear its due share of burden towards contributing to the national exchequer for enriching the life of the people at large. The industrialists and technologists have much common task in this context and it is my earnest prayer that they would not be found wanting in giving this industry its proper place in the future industrial set up of our country.

In the end, let me express a hope that the Oil Industry in India, does not remain confined to milling only, but expand to the fullest of its potentiality. With the enthusiasm observed amongst the technicians and also the industrialists I do not think my hope is farfetched. Of what I have seen of the Oil Industry and its developments in the Western Countries, we in India with all the raw materials at our door, are still in the preliminary stage and have yet to develop the allied industries such as soap, plastics and also find ways and means for the utilisation of all the bye-products of these industries to make our products competitive compared to foreign products.

Gentlemen, with the help of the young technicians of our country, I am sure we shall make big strides in the near future. Let me assure you on behalf of my Chamber that you can rely on our fullest support and co-operation in the effort.

PRACTICAL WORKING AND ECONOMICS OF A MODERN SOLVENT EXTRACTION PLANT

BY

H. V. PAREKH

The Bhavnagar Chemical Works (1946) Ltd., Vartej (Saurashtra).

The Solvent Extraction Plant about which I am going to speak to you, is a semi-continuous batch type extracting unit, almost entirely automatic in its working.

The plant mainly consists of four unit processes, namely, (i) crushing the seeds, (ii) the actual process of extraction wherein the oil is dissolved and carried away by the solvent (iii) distillation of the oil bearing solvent so as to separate and recover the solvent and oil and (iv) to treat the deoiled cake by drying and pack the same in bags.

Raw oil cake as obtained from expellers, rotary or bullock driven *ghanies*, is first broken into small pieces in a machine, in which knives are fixed on a drum which rotates in an enclosed casing. The small pieces thus formed are conveyed by a chain elevator to a raw cake storage bin. From this bin, oil cake pieces, the flow of which is regulated by a damper, fall by gravity over the magnetic separator. This device removes any iron pieces present in the raw cake. After passing through the magnetic separator, the cake falls further by gravity into a cake breaker. The function of the cake breaker is very important, as the final size of the cake as produced in it greatly influences the rate and degree of extraction.

From the cake breaker, the meal is conveyed and dumped into a stationary hopper placed at a high level in the extraction house. From this hopper, the prepared meal is dropped into a travelling hopper in required quantity, for charging into the extractors.

The main process, that is 'extraction', is carried out in five vessels known as 'Extractors'. These extractors are installed in series and at any given time one of them is either being emptied or charged.

In actual operation, the principle of counter current is used. To begin with, all the five vessels are charged with the prepared cake. Fresh solvent is pumped into No. 1 vessel and when it is full, a valve connecting it to the next one is opened and solvent pump continues

its work, till all the vessels are full. As the solvent arriving in No. 5 vessel has during its travel come into contact with cake, altogether five times, it is strongest in oil content and is, therefore, taken into the filter. No. 1 vessel which has had altogether 5 washes is ready for draining and for being put out of working. No. 1 is, therefore, drained from the bottom and is ready for steaming.

The oil bearing solvent is called Miscella, and the richest miscella after filtration goes to a settling tank and thence overflows into a horizontal storage tank called miscella storage tank, from where it is pumped by another steam driven pump to a head tank situated at the highest level in the extraction distillation house, to ensure a constant head in the distillation section.

The miscella, then passes through a heat exchanger into a big vessel, known as Prestill. In this Prestill, the miscella is heated by closed steam to a temperature which is 5°C higher than the initial boiling point of the solvent, employed in the process. This initial heating produces a great foaming of the miscella and hence ample space is provided in the Prestill. After passing through this Prestill, the miscella which has lost part of the solvent, travels further into the calendria, situated at the top of the distillation column. Here, 95 per cent of the solvent present in the miscella is vaporised on the falling film type of evaporator. The last traces of the solvent remaining after through the calendria, are removed in the distilling column of the still, by means of open steam.

The meal in the extractor contains a large volume of very weak miscella, which is drained by the pump and the adhering miscella in the meal, is steamed off with the help of open steam below the false bottom in the extractors.

The steaming of the extractor is stopped, as soon as the test cock, mounted on the top of the extractor, does not show the odour of the solvent. After the steam is stopped, the top manhole of the extractor is opened and any steam inside, is let off into the atmosphere. The bottom manhole is then opened and the stirrer of the extractor is set in motion.

The deoiled cake, known as 'Lex' is forced out from the extractor, by the lower arm of the stirrer moving inside the body of the extractor, while the upper arm of the stirrer pushes top lex to the bottom. The lex pouring out is almost like a sand, provided that the cooking is carried out to its logical end. The successful operation of the stirrer is one of the most important features and requires correct manipulation.

All the condensates in the extraction house go to a big cylindrical tank, known as water decanter. The function of the decanter is to separate out water and solvent.

In order to reduce the solvent loss, down to a minimum, a refrigerating system is provided. All the vents from the condensers and vessels are connected to a vapour duct which opens out at the bottom of a spray tower, filled with reaching rings and through which cooled brine is circulated.

The wet meal coming out of the extractor is conveyed by the belt conveyor to the first floor of the drying house.

The drier consists of an enclosed chamber within which a tube reel is rotated. The wet meal coming through the screw feeder, is allowed to fall on the hot steam tubes of the rotating reel and gets dried and is progressively driven to the other end by paddles provided on the reel. Finally, the dry mass further falls into a schute connected to the suction end of a blower, which conveys it to a dust cyclone placed at the top of a big hopper in the bagging house. At the bottom end of the hopper, an automatic weighing and bag filling arrangement is provided.

We have so far largely treated groundnut oil cake and as India is largest producer of groundnuts I shall mainly deal with the cost of the solvent extraction of groundnut oil cake.

The average consumption figures for the groundnut oil cake are as follows :—

Basis	...	...	...	24 hours.
Working days	...	...	...	300 days.
Capacity	50/55	tons	oil cake	per day.
Electricity...	...	...	...	1000 KWH
Steam	...	...	...	60 tons.
Solvent loss	...	...	...	150 gallons.

The cost of production including labour, depreciation etc., comes out to be about Rs. 60/-per ton of oil cake treated. If working days fall to 250 in a year, the cost per ton will be Rs. 70/-.

The deoiled groundnut meal, which is used as manure, is a much better fertilizer than ordinary oil cake, deoiling by the solvent extraction method, not only makes the recovery of the oil from the cake, a profitable business, but it renders the cake richer in protein percentage and makes the nitrogen easily available for the soil. Residual oil in the ordinary oil cake, forms an oily cover around the protein particles, which is held responsible for the delay caused in the plant germination process.

Experiments carried out by the U.S. Department of Agriculture, regarding the nutritive value of groundnut cake, have led to the conclusion that solvent extracted groundnut meal has the same nutritive value as protein supplement, as pressed groundnut cake meal.

The deoiled groundnut cake is superior to cake containing oil, as a supplement to stock feeding. This is mainly because of the fact that the cooking carried out with steam, during the process of deoiling, renders the protein in the most desirable form, for the cattle feed.

Very meagre literature has so far been published as regards ideal methods for the production of groundnut meal, suitable for human food. The best method by far, to produce quality oil and also the residual oil cake for human consumption, is to treat nice clean cuticle (red skin) removed seeds in expeller running under low pressure, technically known as 'first pressing' or in rotary mills or in *Ghanies* driven by bullocks. The oil obtained by this gentle treatment of seeds is of very good quality. The resulting oil cake, containing about 18 to 20 per cent oil by weight is then defatted in a modern and efficient solvent extraction plant, working under hygienic conditions.

There is a very bright future in India for the preparation of groundnut cake flour, by expeller or village *Ghani*-cum-Solvent Extraction method, for use as human food, supplement to wheat and other cereal grains. Every year we have groundnut crop of 30 lacs tons. If this entire crop is expelled and then extracted under hygienic conditions, it is possible to get 11 lacs tons of groundnut cake flour best suited for human food and to get extra about one lac tons of oil valued at Rs. 16/- crores. This oil otherwise goes as waste.

This great national loss must be stopped by the Government by making it at least a rule that only deoiled cake can be used as fertilizer.

THE ECONOMIC ASPECTS OF THE SOLVENT EXTRACTION PROCESS IN THE NATIONAL PLANNING OF THE INDIAN OIL INDUSTRY

BY

DR. N. G. CHATTERJI

Hindustan Development Corporation Ltd., Calcutta.

A critical review of the present world shortage of oils seems to indicate that this has been on account of three major causes namely: (i) increased demand for vegetable oils in Europe and America, where there has been a steady shortage of animal fats; (ii) a substantial decline in the world production of these essential commodities; and (iii) a steady increase in internal consumption in those countries which were hitherto mostly exporting the same. The trend of events is, however, such that for a considerable number of years Europe and possibly also America shall have to depend upon the far Eastern countries including India for a substantial portion of her requirements of oils. India is, therefore, sure of getting a ready market abroad for any quantity of oil she is able to export and thereby earn dollar exchange necessary for importing capital goods. But on account of the large increase in internal demand she can ill afford to export substantial quantities without inflicting hardship on her own people, so that her participation in the export market would be justifiable only if there is an increase in the production of oil within the country.

Oil production can be increased by growing more oil seeds but agricultural methods are slow in expansion and it is doubtful whether it would be judicious at present to devote any attention to oilseeds at the sacrifice of direct food crops. Under the circumstances the quickest and best results would be obtained by utilising recent developments in the technique of processing oilseeds for increased yield of oil from whatever quantities of oilseeds that are being grown in the country.

The processing of oilseeds in India is at present almost exclusively confined to purely mechanical operations, which even with the most efficient machines put in the market leave about 6 per cent of oil in the cake. As a matter of fact almost one third of the total seeds is in all probability being pressed in bullock-driven *ghanies* which leave about twice as much oil in the cake. In a publication of

the Central Oilseeds Committee issued in December 1950, it has been estimated that about 6,90,000 tons of *ghanie* cake and 12,65,000 tons of mill cake are annually produced in India, so that about 2 lakh tons of oil are being discarded in the oil cakes. Any method by which a substantial proportion of the oil left in the oil cake could be taken out in the form of oil would, therefore, go a long way to meet the problem.

The problem has been solved by a judicious combination of mechanical and solvent extraction processes in the case of high oil bearing seeds and by solvent extraction alone in the case of low ones.

Extracted oil and cake - their quality:

The quality of the extracted oil is just as good, if not better, than expressed oil as has been abundantly proved in the case of the vast soyabean oil industry in Europe and America; soyabean being exclusively treated by the solvent extraction process and the oil used mostly for edible purposes. Indeed the processing of the oil during the after-treatment stage is such that the oil in the finished state cannot possibly contain any trace of the solvent. Extracted cake, however, differs from expressed cake in that the former contains practically no oil. While the superiority of the extracted cake over the other in its manurial value is universally recognised, there has been some difference of opinion in the matter of their use for cattle feeding purpose, based mainly on the question whether the presence of a fair quantity of oil in the cake is an essential requirement for this purpose. Feeding experiments carried out in other countries have been conclusive and it is doubtful if the experiments understood to have been taken in hand in this country would lead to more helpful results.

Extracted cake question-a rational approach:

In the opinion of the writer too much importance has been put on this question of cattle-feed oil cake in this country. It must be borne in mind that the raising of cattle in other countries is mainly for the purpose of human consumption so that the animals should grow as bulky and fleshy as possible. In India this has for all practical purposes no place, cattle being mainly raised for giving milk or for draught. It is very probable that such type of cattle may require only a very small quantity of oil in their daily ration.

Again from all available information it appears that the demand for oilcake for cattle-feed purposes is quite small in this country and it is estimated that the entire requirements of the country for some years to come can be easily met by reserving a small fraction

only of the milled cake. Even in the most exaggerated estimate, it would not exceed the figure of 7 lakh tons of oil cake which can easily be met with that of mustard, *til*, and linseed produced annually by our oil mills. This would still leave the entire quantity of about 10 lakh tons of groundnut cake alone for solvent treatment, not to mention the cakes of non-edible oilseeds like *mohwa*, castor, etc.

Progressive oil millers in this country, who are keen on adopting the extraction process complain, that they find little encouragement from official quarters where the authorities are not agreeable to give the necessary permission to import the plant or facilities for their erection. This attitude is understood to be due to their opinion that the adoption of the solvent extraction process would bring about a scarcity of oil cakes suitable for cattle feeding purposes. However, there are already signs of a certain amount of relaxation in this irrational attitude and applications for import license are not likely to be summarily rejected.

Solvent extraction plant and its economics:

It is not the purpose of this paper to give details of the process, plants, or its economics, as information with regard to these is already in the possession of those that are interested in this matter. The information supplied in the literature sent out by reputable manufacturers of such plants is on the whole quite reliable, as has been varified in the recently erected solvent extraction factory at Bhavnagar, equipped with Bamag plant and working with groundnut oil cake.

The following points may be of general interest :

- (a) The process works most efficiently if the oil content of seed or cake is between 15 and 20 per cent.
- (b) The most economic way of working has in most cases been found to be that wherein the oil content of the extracted cake is about 0·8 per cent.
- (c) With modern plants equipped with solvent recovery system the loss of solvent can easily be kept well within 1 per cent.
- (d) 50 tons per day is the stage above which the continuous plant starts to become more economic in working costs.

(e) An approximate idea of the costs etc. of a 50 tons plant may be had from the following :—

Plant at site.....	Rs. 9,50,000/-
Auxiliaries, Water, Steam, Electric services	„ 8,00,000/-
Factory buildings, boundary walls, drains,	„ 3,25,000/-
Land and Staff quarters.....	„ 2,75,000/-
Stock of solvent.....	„ 50,000/-
Working capital	„ 5,00,000/-
Reserve for purchase of cake, if necessary	„ 5,00,000/-
Total Capital investment	„ 34,00,000/-

(f) The overall processing cost for 1 ton of cake would come to about Rs. 80/-

Concluding remarks.

There had in the past been a certain amount of scepticism regarding the suitability of the solvent extraction process in India. Recently a number of oil millers have returned after investigating for themselves the working of the process in Europe and America and are now quite convinced that the process would also be admirably adaptable in their own country.

Lastly the writer is of the opinion that by the adoption of the solvent extraction process an admirable bridge of reconciliation can be raised over the present gulf between the advocates of oil *ghanies* and presses, for while cakes obtainable from even not very efficient *ghanies* would be ideal for the extraction plant, the working of the mills would in many cases have to be adjusted to produce cakes containing at lest 15 per cent of oil to feed the extraction plant.

SOLVENT EXTRACTION.

BY

L. W. RICHARDS*

Chemical Engineer, Bombay.

In dealing with this subject I intend giving a brief resume of the process: firstly, the various types of plants; secondly, the meal products; thirdly, the oil products.

The demand for oils in Europe for both edible and industrial purposes led to the examination as to whether more oil could be recovered from the seed or cake. This led to the solvent process for the extraction of oil from the cake. An indigenous solvent was developed previous to the 1914 war. These early developments were essentially of the Batch type.

The principle is essentially diffusion. Once the solvent diffuses into the seed and has absorbed its maximum oil content, if the seed is allowed to remain in this condition for any length of time, little or no oil would be absorbed; however, by replacing this mixture by fresh solvent the process repeats itself, the solvent soaking deeper and deeper into the oil bearing material. From these tests it was developed that the material to be extracted should be in such a form that the solvent could readily reach all the parts of the material and flakes were found to give the best results.

In the early type of plants only one vessel was used and the solvent was added in various batches and drained into separate tanks. The oil rich material being washed first with solvent containing the highest oil content and repeated with solvent containing less miscella until the material was washed with clear solvent giving an oil-free material. This was rather laborious and by increasing the number of vessels, they developed what is known today as the semi-continuous batch method.

In the early 1920's the continuous process was developed. The chief of these extractors are the Bollman and Hildebrandt type in Germany and the Bonotto type in Italy.

* In the absence of the author the paper was read by Dr. R. J. Rathi, Poona,

The Bollman type is a large steel vessel with a continuous chain of buckets perforated on the underside into which the cake is loaded on the right-hand and is immediately soaked with a fixed number of gallons of weak miscella of solvent and oil. The miscella soaks through the meal and is discharged from the perforated channels from where it passes on to sprays and washes the cake in the bucket travelling below. Further charges of miscella are passed into the buckets as they descend. This oil rich miscella collects in the right-hand compartment of the extractor and is pumped after filtering to the distillation section.

The buckets in their upward travel meet a solvent which contains very little oil and are gradually washed free of oil as they travel upwards, the final washing being with fresh solvent. This solvent-miscella as it is called is then pumped to the right hand side of the tank to meet the oil-rich cake. The bucket continues its travel and the meal is emptied into a screw conveyor which carries it to the drying chamber. The drying chamber may be fitted with, or without vacuum depending upon the circumstances for which the meal is required. By external heating the solvent is driven off and the meal passes along by a screw type of conveyor in various passes.

The Hildebrandt type is similar to the letter "U"; with 3 legs of the "U" being fitted with screws and baffles to retain the meal in position. The meal passes down the left-hand leg to the "U" along the bottom and upwards on the right-hand side. The solvent produces countercurrent along the right hand side and passes along the bottom and upwards into the oil rich cake on the left-hand leg. The treatment of the oil and cake after this stage being very similar.

In the Bonotto process the meal travels downwards through a tubular conveyor fitted with baffles in which there is a slot and solvent rises countercurrent to the meal travelling downwards.

The Anderson and Allis-Chalmers plants are merely variations of the Bonotto unit.

The Americans met with very little success with the solvent extraction process at first because they endeavoured to treat the oilseed direct. This led to huge volume of solvents being required for the various conditions of the meal which affected the acid values and today they have reverted to the original German method of first reducing the oil content to a figure of 20 per cent by pressure then treating the cake by solvent extraction.

The Americans have developed many modifications of the original Bollman plant such as converting from the vertical to the horizontal type and instead of having a chain of buckets, a circle of compartments such as the French oil mills and Blaw-Knox.

The original solvents used were of the indigenous type mainly, hydrocarbons from Germany and carbon disulphide from Italy. These led to various impurities in the oil and meal which were difficult to remove.

The first solvent extraction plant to come to India was erected in 1911 in Calcutta. This plant suffered the drawbacks of the early solvents.

Another solvent extraction plant of the Merzh type which is really a large soxhlet type was brought to India and originally erected for Dupah seed on the Malabar Coast by a German firm which closed down when they were interned during the 1914 war. This plant was later removed to Kalyan where it is still working.

When I first examined this question in 1946, the only solvents available in India were a 60/120°C cut petroleum fractions. For this higher temperatures are required to be maintained in the plant to rid the oil and cake of the solvent and the resultant products are not as good as one would desire them to be.

The unfortunate experiences of these plants have led to solvent extraction having a very bad name in India. But in Europe and America the development of lower boiling point fractions such as Hexane 60/80°C and Heptane 90/95°C have enabled the solvent extraction process to be more successful.

Meal :

The improvement in the solvents naturally led to improvement in the quality of the meal and the results were still further improved with the development of the Continuous extractor. It was found in the batch process that the large amount of steam which is required to remove the solvent from the meal also affected the condition of the proteins contained in the meal, especially in the case of groundnut and cottonseed, and it was this fact possibly more than the question of labour that led to the development of the continuous process. However, it has been found that the oil and cake produced by the old cold pressing processes such as the hydraulic press in Europe and the *Ghani* in India, generally give a better grade of oil than that produced by the expeller, which requires a higher temperature to enable a larger quantity of oil to be extracted from the meal. It has now been proved that by using a lower temperature in the expelling leaving 15 per cent oil in cake and then solvent extracting, the protein qualities of the meal are very much improved and higher protein values are obtained when the meal is used for industrial purposes.

The meal produced in either the Batch or Continuous process can be used very successfully as an *Organic Fertilizer* of which India requires very large quantities and as there is over a million tons per year of cake available, the potential value is very great.

If the meal is required in its final stage for cattle feeding, then it is an advantage to toast the meal as this gives it a slightly improved flavour and more appetizing to the cattle. In the case of cottonseed and linseed, this toasting not only improves the flavour but also detoxifies certain components contained in the cake.

Oil :

As mentioned before, in the early stages the oil from the solvent extraction process contained various impurities but with the improvement of the better grade solvent available to-day, a better grade of oil can be obtained by the combination of the pressure-solvent process than by the pressure process alone.

The present method of recovery controls the temperatures which affects the oil very quickly and impurities such as phosphatides which are extracted from the cake by the solvent can be very repaidly extracted from the oil by washing with water and clarification. In the case of cottonseed the colour is much improved. The oil must be refined before further use.

The working cost including depreciation in a modern Solvent Extraction plant is about Rs. 70/- per ton for a 25 ton plant and this is reduced to Rs. 55/- on a 100 ton plant with 8 per cent of oil recovered, say 160 lbs. of oil @ 12 as. per lb. that is Rs. 120/- per ton. So the plant shows a handsome return, as well as prepares a better organic fertilizer, a forerunning of new industries and more food.

DISCUSSION

(*On solvent extraction*)

Dr. S. A. Saletore, Assistant Director, Central Laboratory, Scientific and Industrial Research, Hyderabad gave a note of caution regarding the putting up of solvent extraction plant in India because the plants that were previously installed in the country did not meet with success and had to be closed down due to various reasons as high cost of plant, high cost of solvents as compared to America, lack of technical skill and unsatisfactory design for Indian conditions. Question of complete removal of the solvent from the oil and its colour were other points for consideration. He considered the solvent extraction still in the experimental stage in India.

Dr. N. G. Chatterjee, gave the history of the solvent extraction plants in India about which Dr. Saletore referred. The oldest and probably the first designed solvent extraction plant in the world was that erected at Kalayan. It was an exact replica of Soxhlet apparatus. In the absence of the proper solvent, it had to be worked on petrol in the beginning. The second plant installed near Lilloha was brought to India in 1906 or 1907 but as far as he remembered it never worked even after it was erected. Then it was removed from there and put up at Kanpur. There the speaker with his students at Harcourt Butler Technological Institute worked on it with petrol, the only solvent available at that time. One of the greatest difficulty in the plant was that the stirrers used to get bent during working. The plant at Lilloha was the one put up by Bamag but its proprietor was more interested in seeing that it might never work because he could get more money by way of damages than in its working.

Mr. Parekh pointed out that in the economics of the solvent extraction plant the ratio between the prices of the oil and the cake had always to be considered. It always remains at about 6 to 8 times. The actual price of the cake would not matter. He further maintained that the solvent extracted oil after refining was quite suitable for human food and was very light in colour.

Dr. R. J. Rathi remarked that the plants in America were run on more economic lines than in India. One of the greatest difficulty in this country was that the industrialists were speculative. They would wait till the prices of seed go up when they would sell them as such rather than to extract the oil.

In the opinion of **Mr. Om Prakash** the greatest draw back in the adoption of solvent extraction plant in India was the large capacity of such plants and further it could be best worked, with large oil expression plants which did not exist at that time in the country.

AVAILABILITY OF PETROLEUM SOLVENTS FOR EXTRACTION OF VEGETABLE OILS

BY

T. K. NAYAR

Representative, Burmah Shell, Poona

As far as we know the first large solvent extraction plant of modern design to go into commercial production in India was the Bhavnagar Chemical Works, Vertej, which started working in September 1950. We offered this concern the choice of two Special Cut Solvent Oils then available from Abadan :—

(1) *iso*Heptane, 80/90°C

(2) *iso*Hexane, 65/75°C

The B.C.W. preferred the former and we decided after correspondence with our Technical Experts in London to standardise on *iso*heptane as the grade most suitable for solvent extraction in India.

The full specification of *iso*heptane as supplied from Abadan was as follows :—

Specific Gravity at 60°F	...	0.733
Initial boiling point	...	78°C
10% Evaporated	...	79.5°C
50% ,,	...	82.5°C
90% ,,	...	86.0°C
Final boiling point	...	93.0°C
Colour Saybolt	...	30
Corrosion B.S.I.	...	Passes
Doctor test	...	Negative.
Aromatics	...	6% by weight.

*iso*Heptane has proved to be entirely satisfactory in the B.C.W's extraction process. A few months ago we recommended this grade to Messrs Jagdish Industries, Porbandar, who have exactly the same type of extraction plant as the B.C.W., i.e. 20 ton capacity manufactured by Bamags.

We also delivered in 1950, 600 gallons to an extraction plant at Kalyan, operated by Messrs. Ulhas Oil and Chemical Industries.

The Department of Chemical Technology, University of Bombay, have recently completed the installation of a pilot model extraction plant, on which Government officials will be carrying out experiments. We have secured the first trial order of 130 gallons for this plant as well.

As far as I know, the above are the only major extraction plants operating so far in India, but there is another pilot plant at Jadavpur which is run under the supervision of Mr. B. Dass, Professor, College of Engineering and Technology Bengal. Prof. Dass carried out tests on *isoheptane* in 1950 on behalf of Government and confirmed in an official report that *isoheptane* was, in his opinion suitable.

When supplies from Abadan were suspended we wrote to our London Principals asking them to make arrangements for supplies of an equivalent grade from another source. We have now received advice that the only equivalent that can be offered from any source is Benzsol 65/85°C, available from New Orleans, U.S.A.

Unfortunately, it is not at this stage possible for us to quote a firm selling price in India for Benzsol, but we will do all we can to make our price fully competitive. Our London Technical Experts have confirmed that in their opinion Benzsol 65/85°C, should prove to be just as efficient in solvent extraction processes in India as *isoheptane*.

You would probably be interested to know whether Special Cut Solvent Oils are available from indigenous production. The position is that until the middle of 1950 the Assam oil Company's refinery at Digboi, Assam, produced a limited quantity of solvent oils, one of which, 75/95°C, was a fairly close equivalent to *isoheptane*. Most of Digboi's solvent oil production, however, was absorbed by our Calcutta and Delhi Branches, the very long haul making supplies to Bombay area an uneconomic proposition. The latest position is that due to certain operational difficulties Digboi's solvent plant is temporarily closed, and it is impossible to say when fresh supplies will be available from that source.

As far as Burmah-Shell is concerned, therefore, the only grade that we can now offer for solvent extraction in this country is Benzsol from U. S. A.

I have endeavoured in the course of this short speech to indicate in broad lines the availability of Special Cut Solvent Oils for solvent extraction of vegetable oils. In case any further technical details are required by you, I would request you to write to our

Bombay Office. (address :— Burmah-Shell Oil Storage and Distributing Co. of India Ltd., Burmah-shell House, Ballard Estate, Post Box 193, Bombay 1)

INFORMATION

The Chairman informed that Standard Vacuum Oil Company Bombay, had approximately 28,000 gallons of a special petroleum solvent for oil extraction, named Pegasol 1222 at Rs. 2-6-3 per gallon packed in barrels of 35 gallons f.o.r. Bombay. Its characteristics and that of Heptane are given below :—

	<i>Pegasol</i> 1222	<i>Heptane</i>
Sp. gravity at 60°F/60°F	0·692	0·729
Aniline cloud point, °F	—	131
Vapour pressure (lbs. per sq. in.)	—	1·3
Flash point, °F.	below 0	below 0
Colour saybolt	26	25
Initial Boiling point, °F	136	207
10% recovered, °F	—	208
50% " "	160	210
90% " "	178	212
Final boiling point, °F	194	214
Recovery %	98	—
Doctors test	Neg.	Neg.
Corrosion test	passes	passes
Aromatics	5·7	—

EXTRACTION OF CASTOR OIL THROUGH AQUEOUS MEDIUM

BY

J. P. VERMA*

National Chemical Laboratory, Poona.

Oil seeds, nuts and other oil bearing materials consist of liquid fat and solids composed of proteins, fibrous and colouring matter etc. The extraction of oil from the cellular structure of the seeds without increasing free fatty acid content, undesired colour and odour in the finished product can be achieved if the solid portion could be caused to dissolve or separate from oil in an aqueous phase. Then the problem of extraction could be reduced, to the separation of a liquid fat phase from the aqueous phase and solid, at the bottom.

The Russians have employed this water extraction method for the production of vegetable oils by a process known as the Skipin process. This process is claimed to be economical and is in common use in Russian oil mills. The process is worked at a critical temperature and at somewhat high moisture content of oilseeds like cotton seed, sunflower, sesame etc. The yield of oil is about 50 per cent of the originally present in the oilseeds. The process depends upon the selection of particular conditions under which there is maximum selective wetting of the solid seed surfaces by water in preference to oil. The method is used for the preliminary extraction of the oil and is claimed to increase the capacity of the oil mills.

With these ideas in mind a series of experiments were carried out to extract oil of high quality from the seeds economically and in a simple way. As a result of numerous experimentation a process has been evolved which is described as follows :—

The seeds are roasted and then crushed to a fine meal. The crushed meal is digested with 5 to 10 per cent powdered common salt with sufficient quantity of water, for about half an hour at a temperature of 50-100°C with occasional stirring. At this stage lime water containing 0.1 to 0.5 per cent lime on the weight of the seed meal is added in portions during 15 to 30 minutes with continuous stirring. Then potassium nitrate 0.2 per cent by the weight of the

* In the absence of the author the paper was read by Dr. S. L. Sastry, N.C.L., Poona.

seed meal is added with stirring and after 15 to 30 minutes almost free oil is liberated from the mass which is removed easily by decantation or by means of a perforated false bottom. About the same volume of hot water or a little more is then added and after a little boiling and stirring more oil is released which is also separated as above. In this way most of the oil is separated and any moisture contained therein is removed by heating up to 120°C and filtering.

The remainder of the oil is obtained as emulsion by adding enough hot water, stirring and leaving it to settle. On cooling the top layer containing the emulsion is separated. The contents are reboiled with 3 per cent saline water and again allowed to settle and more emulsion is separated. The oil is obtained by heating the emulsion to evaporate off the water and then filtering; or the emulsion can be broken by processing it through a centrifuge and then separating the oily layer. The total yield of oil was found to be 44 per cent on the weight of the seed meal, when the total oil originally present was 47.5 per cent. The chemical constants of castor oil thus extracted were as follows:—

Sp. Gr at 15.5°/15.5°	= 0.9639
Acid value	= 4.4
Saponification value	= 179
Iodine value	= 86.1
Acetyl value	= 147.0

This process can also be worked out with the help of steam alone or with the help of salts, acids, bases, or demulsifying agents.

About 500g. of clean castor seeds are roasted for 15 minutes in a dish and then crushed to a fine meal. 500g. of the seed meal is taken in a flask of about 5 litre capacity and to this is added powdered common salt and 250 c.c. hot water and the contents heated at 50-100°C with occasional stirring for half an hour. Then 0.1 to 1 per cent surfactants in 250 c.c. of hot water is added and the contents stirred and blown with steam under ordinary pressure for 1½ hours. At the end of this period the contents are taken in a separating funnel and the oil water emulsion which comes at the top is separated. The residual meal is washed three times with 3 per cent hot saline water and the emulsion separated as above. The oil is obtained from the emulsion by heating it to 120°C. to evaporate off water and then filtering it. The emulsion can also be broken and oil recovered by working it through a centrifuge. The total yield of oil is found to be 38 per cent on the weight of the whole seed meal.

A series of experiments were conducted using wetting agents like zephiran, aeroseol etc. 500g. of roasted castor seed meal obtained as above was digested in 50 c.c. of water for half an hour, at 80-90°C, with occasional stirring in a 5 litre flask. To this was added 1.5 c.c. of a solution containing 10 per cent zephiran and 90 per cent inert ingredients in 500 c.c. of water and the contents steamed for $1\frac{1}{2}$ hours. At the end of this period the oil-water emulsion was separated by means of a separating funnel. More emulsion was obtained by repeated washing with 3 per cent hot saline water. To the residual meal together with aqueous portion, 1.5g. of aerosol was added and the contents reboiled, on settling in a separating funnel more emulsion was obtained. The contents were again washed with hot water and the emulsion separated as above. Oil was obtained from the emulsion by heating it to 120°C and then filtering it or by working it through a centrifuge. The yield of oil obtained was found to be 38 per cent on the weight of the seed meal.

COMMENTS ON EXTRACTION OF CASTOR OIL THROUGH AQUEOUS MEDIUM

BY

DR. S. L. SASTRY

National Chemical Laboratory, Poona.

The results of the aqueous extraction of castor oil on a laboratory scale encouraged us to experiment on larger batches. The process consisted of seven main steps, 1. Cleaning of the seeds, 2. roasting, 3. coarse grinding, 4. fine grinding to charge consistency, 5. cooking and separation of oil, 6. emulsion formation and 7. emulsion breaking ; removal of water.

Each of the above steps were applied for the extraction irrespective of the scale. The largest scale attempted was $\frac{1}{2}$ cwt., and the smallest was 15 lbs. Throughout the course of work variations were made with a view to save time, labour and costs.

One of the runs that may be considered typical was conducted in the following manner :- The seeds cleaned pneumatically were roasted in a steam jacketed cast iron pan by condensing steam at

60-70 p.s.i., and taken through a coffee-mill grinder. The coarse meal so obtained was ground to a fine meal between rolls and charged into a steam jacketed pan. The required quantities of water and common salt were added and the mass was heated by steam at 40-50 p.s.i.g. After addition of lime water and surface active agent the liberated oil was removed by applying vacuum and collected in a trap. A second extraction of free oil was made by addition of more water and heating. After this stage it was difficult to remove free oil from the mass by vacuum alone and the remaining quantity of oil was removed as emulsion, by adding a large quantity of water and heating. The emulsion was boiled until all the water was removed. After it reached a temperature of 120°C the clear oil was separated from the solids remaining at the bottom. The solids, however, held up some oil and we shall refer to this mass as emulsion slurry. The yield of emulsion slurry was once as high as 0.4 lbs. per lb. charge and by careful control of conditions this was reduced to about 0.02 lbs. per lb. charge. This reduction will mean a thin recycle stream and considerable steam saving in a production schedule. The oil obtained was straw yellow in colour and a sample of oil from one of the runs did not have toxic effects on test animals.

In Table I are recorded the percentages of extraction expressed on the basis of the weight of meal charge, and as total percentage extraction, defined as the per cent of the total available oil extracted.

TABLE I

Run	Scale	Oil in the seeds %	Extraction on the weight. of meal charge %	Total extraction. %
Laboratory Experiment	500 g.	47.5	43.0	88.1
1.	15 lbs.	47.5	34.3	70.3
2.	15 "	47.5	42.2	86.5
3.	15 "	47.5	43.0	88.1
4.	$\frac{1}{2}$ cwt.	47.0	41.4	85.8
5.	$\frac{1}{2}$ "	46.2	43.4	93.2
6.	$\frac{1}{2}$ "	46.2	40.8	87.5

DISCUSSION

Dr. R. J. Rathi wanted to know from Dr. Sastry whether the oil would not deteriorate by heating it or its emulsion at 120°C , because in certain cases in the solvent extraction, the oil was found to deteriorate even when heated at 95°C .

Dr. Sastry replied that in the beginning the oil emulsion remained at 100°C till the moisture was entirely removed and then kept 120°C only for a very short time. The temperature was not allowed to rise above 120°C . Further if steam be used the danger of the spoilage of the oil was still avoided.

Mr. Om Prakash wanted to know whether the acid value of the expressed oil was compared with the aqueous extracted oil.

Dr. Aggarwal informed that the acid values of the solvent extracted castor oil and that obtained by the present method were found to be almost identical.

Dr. K. S. Murthi, Principal oil Technologist Institute, Anantapur wanted to know the percentage of oil extracted by the aqueous process and that left in the cake in the case of groundnut.

Dr. Sastry replied that the results of groundnut were not available. But in the case of castor about 7 to 10 per cent remained in the cake while 88 to 90 per cent was removed.

Mr. Om Prakash pointed out that the difference of yields of oil between the different samples was rather high.

Dr. Sastry informed that lower yield was obtained only in the first experiment and the average yield of the oil could be taken as 90 per cent.

Prof. McBain remarked that the experiments for establishing the correct yield were still in progress.

SOAP AND GLYCERINE

THE COMMERCIAL AND ECONOMIC ASPECTS OF THE INDIAN SOAP INDUSTRY

BY

DR. ING. B. P. GODREJ

Godrej Soaps Limited, Bombay.

The Soap Industry is an important branch of the chemical industry. Notwithstanding the fact that the Indian chemical industry is still in its infancy, this branch is highly developed, the reason being that the start was made very early and the private enterprise which runs this industry is progressive minded. The equipment possessed by the major soap factories is good. Some factories have installed up-to-date plants for certain processes, which are considered innovations even in technically advanced countries like the U. S. A. and the U.K. When new efficient processes are adopted, sometimes unforeseen difficulties are encountered, and therefore it is necessary to have a comprehensive research department in order to overcome these difficulties. In my opinion, automatic plants are pre-eminently suited to Indian conditions to ensure steady output. Experience of conditions prevailing in our country should influence our choice of plant and machinery. When selecting a plant, the corrosion of equipment to be expected by adopting a certain process should be given due consideration. Automatic controls are not only conducive to less dependence on labour, but also ensure steady output and better quality of products. The conventional soap boiling procedure, at least the finishing operation known as "fitting" must be looked upon as an "art". The present-day developments, especially in the direction of continuous automatic plants employing scientific controls at every stage, have raised the status of the soap industry,

The Commercial aspects of the Indian Soap Industry :

I have already pointed out that all the major Indian producers of soap have well-equipped plants. All of them have planned to operate on a large enough scale to bring down unit costs. Notwithstanding this fact, the present margin of profit in this industry is very low. This is mainly due to the very high prices of by far the most important raw material, viz., glycerides. At the present moment, raw materials constitute as high as 70 per cent of the cost structure, and taking into consideration that all the major factories

are well-equipped, possess technical know-how, and are in the position to operate on a large enough scale, there is nothing else they can do to bring down costs. It is too well-known that the purchasing power is limited, therefore, prices cannot be raised without sacrificing sales. The only thing that can be done to infuse a healthy tone is to explore the possibility of bringing down the prices of raw materials. The important raw materials are coconut, *mowrah*, and groundnut oils. At present the duty on imported coconut oil is 44 per cent ordinary and $31\frac{1}{2}$ per cent preferential for import from Commonwealth countries. In most countries, the duty on imported raw materials is nominal, in some it is not levied at all. Although we are so near the producing centres, coconut oil costs more here than, for example, in the U.K. or in the U.S.A. Now, as India is a producer as well as an importer of coconut oil, the Indian plantation owners are naturally interested in the continuance of this high rate of duty, whereas the soapmakers have made out a case long ago for the abolition of this duty. The idea underlying this protective duty was to afford protection to the indigenous growers against foreign competition. But the duty has not served its purpose, as the methods of cultivation adopted in India for growing coconuts are still primitive so that the yield per acre is most unsatisfactory, and the acreage under cultivation which was expected to increase, is still more or less the same. The fact that a high rate of export duty is levied by Ceylon goes to prove further that profiteering is indulged in by the local vested interests at the expense of the soapmakers. The Indian Soaps and Toiletries Makers' Association has made repeated representations to Government in this behalf directly and also through the medium of different Chambers of Commerce and similar organisations. In spite of the fact that the Deputy Minister of Industry and Commerce was recently reported to have declared that 1950 was a bad year for the soap industry, Government have still not taken any action in this matter. Quite a number of soap factories have closed down of late, as a consequence of which the installed capacity has considerably fallen. Our soap exports are at present practically nil on account of the low demand as a result of high price for the reason already indicated. Reports from our Trade Commissioners clearly state that we cannot compete at our present prices. I wonder whether our Government have investigated the possibility of getting more revenue in the form of income-tax from soap factories than by levying this import duty.

The other important oil used by Indian soapmakers in large quantities is *Mowrah* oil. Although it is generally considered non-edible, its price is very high at present. The main reason for the high price is low production. It is said that during the previous prohibition

campaign, many *Mowrah* trees were cut down, because *Mowrah* flowers can be used for making alcohol. The suggestion made by the All-India Soapmakers' Association, to plant *Mowrah* trees on road sides, is worth implementing. If *Mowrah* oil of low f. f. a. is available in the market, it could be upgraded by refining, bleaching, deodorizing, and slightly hydrogenating it in order to make it stable against rancidity. Such upgraded oil could be used for making toilet soap possessing excellent solubility, hardness, lathering, and keeping quality. Unfortunately *Mowrah* Oil of low f. f. a. is at present seldom available. There are quite a number of other Indian nonedible oils which can be used for soap making, but it is unfortunate that none of them can be used in their natural state because of their dark colour and obnoxious odour.

When considering the possibility of using other than the well-known oils for soap-making, chemical characteristics of the oils should be carefully studied. Thus, an idea of the expected properties of the resultant soap can be formed. If an oil appears suitable from the technical point of view, the feasibility of using it from the commercial point of view should be considered. To do this successfully, it is necessary to have a clear idea of the minimum quality requirements of the finished soap. Accordingly, it should be determined whether all of the following operations: refining, bleaching, deodorizing, and hydrogenating or say, only the first and the last need be undertaken to upgrade the oil.

It will be seen from these remarks that the price factor comes in the way of effective utilization of our natural resources. If Government should sponsor a scheme for economical collection and distribution of suitable oilseeds, there is no reason why we should not succeed in making the most of the wealth which nature has liberally endowed us.

Another oil used extensively for soapmaking is groundnut oil. It is used in the raw state as well as after hydrogenation. Its price has risen so steeply in recent years that it is now seven times its pre-war price.

From the point of view of cost, caustic soda is the next important raw material. The indigenous production is increasing day by day, but is still not sufficient to meet the entire requirements of the country. The sodium hydroxide content is lower than that of imported caustic soda and the percentage of sodium chloride is higher. This raises the sodium chloride content of the finished soap, which has two deleterious effects in toilet soap, viz., sweating and cracking, which offer sales resistance. The only remedy against cracking of a soap of a given sodium chloride content is to soften it by lowering

its titre. This is a mere compromise, as a soap which remains firm in the soap dish up to the end is desired. Moreover, considering that India is very warm and about half the year the humidity is very high in about half of the country, it would appear advisable to make toilet soaps as hard as possible without rendering them liable to breakage during rough handling in transit, which is still not uncommon in India. In the Indian Standards Specification for technical caustic soda, there is a remark that it is desirable that the quality of indigenous caustic soda should be improved as soon as possible and to that end a revision of the present standard would be undertaken within three years.

Perfumes are considered indispensable for the manufacture of high quality soaps. Though a toilet soap is used mainly for cleansing, the fragrance in it accentuates the feeling of freshness after a bath. Excessive perfume causes smarting of the skin, and therefore, only a little more than that required for masking the characteristic odour of soap should be used. It should be remembered that the sins of soap boiling cannot be covered by excessive perfuming. Even laundry soap made from good raw materials needs to be perfumed to some extent at least. Most of the laundry soap blends are based on citronella oil. Quite a number of indigenous essential oils like sandalwood oil, palmarosa oil, lemongrass oil, etc. are consumed by soapmakers in large quantities, whereas aromatic chemicals, excepting the isolates of indigenous essential oils, are imported.

Economic Aspects.

Although India has a huge population, it is a poor market for soaps. The annual soap consumption per person in India is only about 12 ozs., while it is 25 lbs. in the U.S.A. and 21 lbs. in the U.K. When considering such statistics, it should be borne in mind that the greater part of India is situated in tropics, and, therefore, if the standard of living had been the same as in Western countries, we could have reasonably expected the consumption per person to be substantially higher. Our National Government is planning to raise the standard of living of our people; therefore, the prospects of the soap industry will depend also on the outcome of these efforts. It is planned to increase the production of caustic soda, soda ash, and soap. Whereas the present production of soap is only 1,02,000 tons against an installed capacity of 2,69,000 tons; it is planned to produce 2,70,000 tons in 1955-56 against an estimated capacity of 2,88,000 tons.

This planned progress can only be achieved, if the Government takes more interest in the industry and removes the heavy and unfair duty on oils that have to be imported from the neighbouring countries.

THE USE OF NON-EDIBLE OILS IN SOAPMAKING IN INDIA

BY

G. FORD AND DR. G. S. HATTIANGDI

*Lever Brothers (India) Ltd., and The Hindustan Vanaspati
Manufacturing Company Ltd., Bombay.*

Raw materials used in soapmaking in India :

The chief raw materials used in the soapmaking industry may be categorized as "hard" oils, "soft" oils and "nut" oils. Since animal fats, such as mutton or beef tallow, are not used for soapmaking in India to any great extent the "hard" component consists usually of a vegetable oil which has been hydrogenated to the required degree of hardness. The vegetable oils which are hardened in India for soapmaking purposes are groundnut oil, linseed oil, safflower oil, sesame oil, nigerseed oil, and, to a certain extent, castorseed oil. Crude unhardened *mowrah* oil is considered by some to fall into the category of "hard" oils.

The chief "soft" oils used for soapmaking in India are groundnut oil, safflower oil and rosin, as well as soapstock and acid oil which are bye products of the *Vanaspati* industry.

Coconut oil is possibly the only "nut" oil used in soapmaking in India.

Edible and non-edible components :

The dictionary definition of the word "edible" is "fit to be eaten as food". By this definition, much of the crude unrefined oils manufactured in India could not be termed as being edible. However, modern refining techniques have made such rapid advances that many oils which might have been termed as being non-edible some years ago are now being processed for edible purposes. Thus, the distinction between "edible" and "non-edible" oils is narrowing down.

In Western countries, crude unrefined oils and fats are not considered to be edible products. In India, due largely to economic circumstances and partly to the acquisition of taste, several oils such as groundnut oil, coconut oil, sesame oil, mustard oil, rapeseed oil, etc. are consumed in the crude unrefined state.

Crude groundnut oil and coconut oil, and to a limited extent sesame oil, are the chief edible oils used by soap manufacturers in India. Cottonseed oil, which is also used for soapmaking purposes, can be processed to give an edible product but currently it is not used in large quantities in *Vanaspatti* and other edible food industries in India.

Linseed oil, *mowrah* oil, castorseed oil, rosin, soapstock and acid oil are the chief non-edible raw materials used in the soapmaking industry.

The average "hard", "soft" and "nut" oil contents of oil charges used by recognised soap manufacturers in India may be reckoned to be substantially equal to one another. Assuming that all the "hard" oils and about two-thirds of the "soft" oils used are non-edible, the edible components of oil charges used for soapmaking may be reckoned to be approximately 25-30 per cent coconut oil and 5-10 per cent groundnut oil. According to the National Planning Commission, about 102,000 tons of soap were manufactured in India during the year 1950-51. On the basis of the above compositions, *ca.* 20,000 tons of coconut oil and *ca.* 7,000 tons of groundnut oil, or *ca.* 30,000 tons of total edible oils may be taken to have been used for soapmaking purposes.

In the absence of more recent data, the following figures are quoted from *The Indian Soap Journal* (17, 8, (1951)) for oil produced in registered oil-mills in India during 1948. It will be seen from these data that even the partial substitution of edible oils with non-edible oils is not feasible currently, because the latter are not being produced commercially.

Oil	Amount of oil (in tons) produced in registered mills in India in 1948.	
Castorseed	...	...
Coconut	...	...
Cottonseed	...	...
Groundnut	...	...
Linseed	...	...
<i>Mowrah</i>	...	...
Rapeseed	...	...
Sesame	...	...
Other varieties	...	...
Total	...	385,850

Substitutes for edible oils, and difficulties entailed in their utilization:

Different investigators have, during the past few years, suggested several non-edible oils as substitutes for the edible oils used in the soapmaking industry. Most of these are "soft" oils. Very few suggestions having been offered in respect of "nut-oil substitutes". It might be well to point out at this stage that the main difficulty encountered by soap manufacturers is not in finding substitutes for "hard" and "soft" oils, but in finding a "nut"-oil substitute.

Considerable data are reported in the literature on the physico-chemical characteristics of the substitute oils. The chief difficulties which arise in their utilisation are as follows :

- (a) The oil-bearing materials (seeds, nuts, etc.) are currently not being cultivated systematically and/or to any large extent; consequently, such materials do not have any commercial significance at the moment.
- (b) Factual data on the quality of the oil-bearing materials with reference to variations in climatic conditions, types of soil, etc. are lacking; consequently, oil-seed crushers are reluctant to produce oil from materials of unknown and/or variable character.
- (c) In the absence of a regular supply of a standard quality of oil, it would be extremely difficult, if not impossible, for the soap manufacturers in India to produce soap of a standard quality.

Many of the substitute oils suggested so far are very heavily coloured and have a deep characteristic odour; further, many of them have a relatively high percentage of unsaponifiable matter, and resinous and mucilaginous matter. It would be virtually impossible to use such oils for manufacturing toilet soaps and high-grade laundry soaps without having to refine the oils quite considerably.

It is felt, therefore, that while efforts are made for the systematic and extensive cultivation of these relatively unknown oil-bearing materials, attempts should also be made to improve their quality and hence the oil.

Alternatively, it is felt that these oils should be split, and that the resultant fatty acids should be utilized for soapmaking purposes.

Conclusions:

In the interest of national economy, there is a genuine desire on the part of all concerned to increase the food potential of the country by substituting non-edible oils for edible oils which are

currently being used for manufacturing non-edible products, such as soap. Unfortunately, the problem of utilizing such oils appears to be going round in a vicious circle, characterized by lack of co-ordination between planning bodies, scientists and economists, oil-seed crushers, and consumers such as soap manufacturers.

It is felt that it is up to an institution like the National Chemical Laboratory, which is fully conversant with the Government's planning schemes and also with the general trends on the part of private enterprise, to break up this vicious circle.

Dr. N. N. Godbole, Director Industries and Commerce, Rajasthan, Jaipur on the subject 'USE OF CHEAP COMMERCIAL OILS IN MAKING SOAP' informed as follows :

Certain cheap oils like *neem*, *karanja* and *polang* etc. are being suggested as cheap substitutes for making soaps. The author paid a visit recently to the soap factory at Modinagar and one at Delhi where such oils have been purchased by tons and are being tried for soap manufacture. It has been found that these oils are good for cheap semi-boiled washing soaps. If, however, they are used for making settled soaps, it has been observed that the soaps get very much decolourised after standing and make the soap ugly and unsaleable. Therefore, in recommending cheap oils for making settled soaps, special work should be done on the nature, the causes of the decolourisation caused in the soaps. Unless this question is solved it would be unwise to recommend the use of the cheap oils for the manufacture of settled soaps.

DISCUSSION

Mr. D. K. Gupta, representative Akhil Bharat Sarva Seva Sangh, Wardha, suggested that the production of soap should mostly be taken as a village industry and oils from minor oil-seeds growing in different parts of the country should only be used in its production. By this plan the villagers would be able to use more soap.

Mr. D. J. Ribeiro, Forest chemist, Bombay State pointed out that minor oil-seeds might not be enough in particular localities. He, therefore, suggested that such minor oil-seeds should be mixed and the oil extracted from the mixture might be used in soap making.

Mr. G. M. Kelkar, of the Village Industries Laboratory, Poona informed that he had been preparing washing soap with *nim*, *Karanja* and *Undi* oils without refining. *Nim* oil in certain cases was treated with sulphuric acid. For masking the colour and odour he added some synthetic dyes and perfumes to finished soap.

THE SWEATING OF SOAPS AND THEIR PREVENTION

BY

DR. N. N. GODBOLE

Director, Industries and Commerce, Rajasthan, Jaipur.

The sweating of soaps in India is a typical problem. A number of toilet soaps when exposed or even when they are wrapped in butter paper begin to absorb moisture from the air and begin to "sweat" in the rainy season. This is specially observed in those parts of India where the monsoon is of a long duration e.g. Bombay, West Coast of India, etc. In places like Rajasthan this phenomenon is not very much known. A large amount of work has been done on this problem by a number of workers. The inference drawn by Godbole and coworkers at the Benaras Hindu University has led to the following conclusions. The greater the percentage of sodium and potassium salts of acids ranging from C_6 to C_{14} and the greater the percentage of sodium salts of unsaturated acids of C_{16} series, the greater the possibility of sweating. Although, therefore, the causes of the sweating are understood, the remedies for preventing the sweating are not yet fully known. The attention of scientists is drawn to this question to find out how this sweating should be stopped. The use of coconut oils is essential in all washing and toilet soaps for its lathering properties.

DISCUSSION

Dr. S. L. Sastry, (N. C. L.) enquired from Dr. Godbole if study had been made on the sweating properties of clay adulterated soap and whether he would consider packing of soap in celophane etc. a good remedy for minimising sweating.

Dr. Godbole replied that celophane was very costly. Soap makers in India use butter paper but that would not help much against sweating. Clay also could not help in reducing sweating.

Dr. K. S. Murti agreed with Dr. Godbole that major cause for the sweating of soap was atmospheric conditions and except for good packing there was no other method of reducing it.

In *Dr. N. G. Chatterjee's* opinion the sweating of soap was due to two reasons. One was the absorption of water which certainly was on account of humidity together with the composition of soap. The other, especially, in the case of bar soaps was due to the change in the physical conditions of the soap that was taking place and which might be called crystalloidal condition. He gave an interesting observation in the case of packing of bar soap in a wooden case covered on outside with water proof paper. It would be found that top layers showed very little moisture, but in between the bars of soap which were in contact with each other a good amount of sweating would be found. So, some change in the physical condition of soap might be taking place which was responsible for sweating. That might be similar to syneresis.

Dr. Godbole, however, pointed that it was not a case of syneresis because during sweating an increase in the weight of soap takes place. Syneresis would not allow an increase in the weight. Moreover, had sweating been the case of syneresis, it should have taken place in dry places as Rajasthan also, but it was not actually the case.

REFINING OF GLYCERINE BY ION EXCHANGE RESINS

BY

DR. H. A. SHAH

National Chemical Laboratory, Poona.

Even though the phenomenon of Ion Exchange was known to the chemists of the last century, substantial progress has been possible only after the discovery by Adams and Holmes of synthetic cation and anion exchange resins. There have been many strides in the applications of ion exchange to various fields other than water conditioning in the last decade, and the refining of glycerol by ion exchange is one of the new chapters in this ever expanding field.

There are several methods for the preparation of glycerol. They are: (1) Saponification of oils and fats for soap production with glycerol as the by-product. (2) The splitting of fats and oils by the Twitchell process for soap production. (3) The synthetic production of glycerol from propylene by chlorination and hydrolysis. However, only the first method is of importance in the context of the indigenous industry.

In the production of soaps by the saponification of fatty oils etc., glycerol is obtained in the soap lye. The soap lyes contain besides glycerol a number of impurities such as salt, fatty acids, metallic soaps, and other organic impurities. These have to be removed for preparing a pure product. The process of obtaining refined or chemically pure glycerine consists of evaporating the soap lyes. During this process, as the concentration of glycerol increases, the solubility of the salt decreases. As a result the salt crystallizes out and is separated from the glycerol. This is one of the first steps in glycerol purification. The resulting crude glycerol is a dark brown viscous liquid containing usually 80 per cent glycerol and 8 to 10 per cent salt. For the preparation of a chemically pure glycerol, this crude product is distilled under vacuum. Redistillation of the product produces a chemically pure glycerol and this is usually the extent of purification by distillation.

Several attempts had been made in the past to make use of ion exchange materials. Schwartz¹ incorporated a zeolite in his process to exchange excess of calcium for sodium after lime treatment and

precipitation. Hoyt² suggested the use of an anion exchanger for removing any free acid present in glycerol solution after saponification and treatment with sulphuric acid to precipitate calcium sulphate. Metzger³ did some work on the removal of acids by treatment with anion exchangers. Bradner⁴ used the ion exchange process for the purification of polyhydric alcohols by the use of cation and anion exchangers for removing reducing sugars. This was accomplished by digestion of the reducing sugars prior to ion exchange. In a British Patent⁵, glycerol solution was successively passed through a plurality of ion exchangers but distillation was still required to produce an acceptable product. Preliminary work on the purification of glycerol by ion exchange was reported by Kahler⁶. However, the most extensive and comprehensive work on the purification of glycerol by ion exchange has been reported by Stromquist and Reents⁷.

The purification of glycerol by ion exchange involves passing a solution of either the spent lye or crude glycerol through successive beds of regenerated cation and anion exchange resins. The ion exchange resins remove from the aqueous solutions the ionized solids, viz. sodium chloride, free fatty acids, the organic acids, etc. During the process the colouring matters are also removed producing an almost water white aqueous solution of glycerol of purity 98 per cent or above. This solution on evaporation, produces a chemically pure glycerin. The ion exchange resins are regenerated with either an acid such as sulphuric or hydrochloric acid, or a base such as sodium carbonate or caustic soda. During the process of passing the glycerin solution through the bed of ion exchange resins, no heat is required for the reaction, nor does the material go through any change of phase as is true with distillation. No large amount of caustic are required to be added to the glycerol to be deionized, to prevent fatty acid carry-over, as is the case with distillation. Instead, these fatty acids and other ionized solids are removed during the de-ionization process.

There are several requirements that must be adhered to before the raw glycerol solution can be fed to the ion exchange units.⁷ They are: (1) The solution must be quite dilute and have a low viscosity so that there is no great pressure drop across the exchanger beds. Usually it is preferable to have a solution with 35 per cent solids or below. (2) The solution must be relatively free from fats and oils as these tend to foul the exchange beds. (3) Turbidity in the solution must be kept to a minimum as suspended solids also hinder and retard the exchange process as well as the incidental colour removal. In case there is an excessive amount of suspended materials in the

crude spent lyes it would be preferable to filter them through an adsorbant such as activated carbon. (4) The temperature of the solution should be low, preferably 95°F, or there about.

A method at present of theoretical interest, but holding considerable promise^a consists of forming a complex anion of glycerol with boric acid or sodium tetraborate. The complex anion is adsorbed on an anion exchanger. A removal of 92 per cent to 98 per cent of glycerol from solutions upto the break through-point of the resins was obtained. Desorption by aqueous solution and organic liquids was tried but the results were not satisfactory. It is possible that if a satisfactory desorption technique is worked out the process could be of use in the treatment of soap spent lyes and sweet waters containing a low amount of glycerol and a high amount of ionized salts.

Economics :

The economics of the process of purification of glycerine by ion exchange depend mainly on the cost of chemicals needed for regeneration and the cost of evaporation. This has to be balanced by the cost of distillation and the loss of glycerine as foots during the distillation process. Hence the cost of the process depends on two factors: (1) the percentage of glycerol in the crudes, (2) the percentage of salt in the crude lyes. During investigations carried out at the National Chemical Laboratory, it was found that for treating crude glycerine containing 80-81 per cent glycerine and about 8-9 per cent salts, the cost of regenerants would be approximately from 0.7 to 1.0 anna per lb. of 99 per cent pure glycerine (unpublished work). The dilution of glycerine will amount to between 2.5 lb. to 4.0 lbs. of water to be evaporated per lb. of pure glycerin. It is our experience that for reducing the costs of regenerants it is desirable to have a minimum ratio of glycerin to salt of 9 is to 1.

Advantages :

The concentrated glycerol produced by ion exchange followed by evaporation is equal to and in most cases superior to distilled glycerol. Glycerol obtained by ion exchange treatment generally has less ash, colour and fatty acids and esters than distilled glycerol. It also has greater stability to exposure to sunlight. However the greatest advantage is that substantially all the glycerol is produced as the C. P. product. On distillation only about 66 per cent of the product is C.P. grade, the rest being Dynamite grade and glycerin foots.

The use of the ion exchange process to purify glycerol and polyalcohols may prove a step towards recovery of these valuable chemicals and is especially worth investigation by new plants going in for recovery of glycerine.

REFERENCES

1. Schwartz, Theo. *U.S.P.* 1,824, 507 (Sept. 22, 1931)
2. Hoyt. Howard. E., *U.S.P.* 2, 381, 055 (Aug. 7, 1945)
3. Metzger, F. J., *U.S.P.*, 2,409, 441 (Oct. 15, 1946)
4. Bradner, John D., *U.S.P.* 2,463, 617 (March 8, 1946)
5. *British Patent*: 633, 343 (Dec. 12, 1949)
6. Kahler, F. *Chem, Eng* 1950, 57 No. 7, 109.
7. Stromquist, D. M. & Reents, A. C. *Ind. & Eng. Chem.* 1951, 43, 1065.
8. Zager S. E. and Doody, T. C. *Ibid.* 1951, 43, 1070.

HYDROGENATION
OF OILS

THE VANASPATI INDUSTRY : A BRIEF SURVEY

BY

A. E. SHOHET

The Hindustan Vanaspati Manufacturing Co., Ltd., Bombay.

In a flash of inspiration bordering on genius, Dr. M. D. D. Gilder, the Minister for Health, Government of Bombay, once brought the volatile *Vanaspati* controversy heavily down to earth by asking a simple man-to-man question. He was speaking in the assembly on a private member's bill seeking to ban the manufacture of *Vanaspati* in Bombay State when he was interrupted by one of those self-appointed custodians of public morals by what to any other Bombay minister might have appeared as a disconcerting query : "Why", this irate moralist wanted to know "can the Government of Bombay enforce Prohibition yet hesitate to ban *Vanaspati*?" Dr. Gilder, the man of science and the student of human nature that he is, fired back : "Will my friend prove that the consumption of *Vanaspati* is as harmful as the taking of liquor? Will he prove that anybody who has been fed on *Vanaspati* has gone home and beaten his wife?" "If that is done, Sir", added Dr. Gilder with devastating non-challenge "We shall step in at once and stop the manufacture of *Vanaspati*" !

This is probably as good a specimen as any of the irrational controversy that has developed round the *Vanaspati* industry in the last 4 or 5 years. Happily the importance of the *Vanaspati* industry is being increasingly appreciated by the general public to-day. To what extent Dr. Gilder's challenge has contributed to the edification of public knowledge one can only guess ; but the fighting speech in defence of the industry which Mr. Munshi, the Minister for Food and Agriculture in the Government of India, recently made in Parliament on Pandit Thakur Das Bhargava's anti-*Vanaspati* bill would indicate that the Government of India have at last decided to prick the anti-*Vanaspati* bubble. In the course of his speech Mr. Munshi not only conceded that the *Vanaspati* Industry is one of the most important industries in the country but also characterised the agitation against *Vanaspati* in the name of the cow as "sloppy sentimentality". Indeed, he bluntly called on the agitators to consider whether "an industry of this magnitude" which "has given such wealth to this country" should

be "destroyed or put a stop to" merely on grounds of "passion or sentiment". Apparently a *Vanaspati* minister, as Mr. Munshi was described, can demolish an emotional argument with *ghee*-like vigour!

Yet a more significant straw in the political wind was Mr. Jawaharlal Nehru's homily at the last Congress session when a non-official resolution against *Vanaspati* was proposed for discussion. According to press reports Mr. Nehru "did not consider the resolution as proper for the Congress session where, he emphasised, they must keep up certain standards with regard to the subjects to be discussed". In other words, in the eyes of the Congress President and Prime Minister a resolution against *Vanaspati* is now too ill-conceived a proposition to be considered by the predominant political party of the country. This shows that political prejudice is at last yielding to the authority of science; and it is a welcome sign, as indeed it is in the fitness of things, that a Symposium of this high level, organised by one of the leading research institutes in the country, should devote part of its attention to the dissemination of accurate knowledge on a subject which should never have been dragged into the arena of public controversy.

The *Vanaspati* Industry is a relatively young industry. It started on a small scale in India after the first world war, but its greatest development was witnessed during and after the second world war. In 1935 the production of *Vanaspati* was 18,000 tons; in 1950 it reached a little over 170,000 tons. In other words, production increased nearly tenfold in the space of 15 years (Appendix I). To-day, next to the sugar industry, it is the largest food processing industry in India (Appendix II). Nearly Rs. 25 crores have been invested into it (Appendix III). It gives employment directly and indirectly to over 60,000 people and as many as 50,000 dealers distribute its products throughout the country. Its contributions to the national economy are appreciable. In 1950 the industry contributed to the Union and State exchequers over Rs. 4½ crores by way of excise, sales tax, town duties, etc. (Appendix IV). The importance of the industry in the national economy has now been officially confirmed by Government by its inclusion in the schedule of industries under "The Industries Development and Regulation Act, 1951". This means that the regulation and development of the *Vanaspati* industry is now exclusively in the hands of the Union Government.

But perhaps the main contribution of the *Vanaspati* industry has been the rationalisation of the fat resources of the country. This calls for a word of explanation. Traditionally, the most popular fat in India is *ghee* and among the oils mustard, til and coconut are best

known. In the northern parts of India people are generally accustomed to *ghee*. In the coastal parts coconut oil is popular and in Bengal, Bihar and Uttar Pradesh preference is for mustard. Til is perhaps the only oil that finds ready acceptance throughout the country. Groundnut oil, however, though a first-class oil for culinary purposes and ideal for processing, has, presumably because of its late arrival on the scene in India, hitherto had little following. It is still considered as "the poor man's oil". By itself, therefore, groundnut oil in its raw form would have continued to be neglected and would not have been able to contribute to the extent it has done to the consumption of fat in India had it not been for hydrogenation. The *Vanaspati* industry has thus made it possible for the oil of the humble groundnut to assume ready acceptance throughout the country by cutting across the regional preference for oils, as in the form of *Vanaspati* it is acceptable and popular all over India. Mr. Munshi, the Minister for Food and Agriculture, concedes that this rationalisation of the fat resources of the country "is the most important contribution that the Industry has so far made".

But this is not all. By encouraging the oil crushing industry to meet the growing internal demand for groundnut oil, the *Vanaspati* industry has helped to retain the oilcake in India. The reduction in the export of groundnut seeds from 12,00,000 tons pre-war to less than 1,75,000 tons to-day has added 4,40,000 tons of groundnut cake to the limited cattle food resources of the country.

Yet another potentially decisive contribution, testified to in the latest "Report in the marketing of milk in the Indian Union (1950)", is the "recent changes in the manner of utilisation of milk" due to the "extensive use of *Vanaspati* in cooking, in preference to *ghee*, which has become prohibitively costly.....". These, to quote the report further, are "developments in the right direction as producers always get a better return when they are able to sell their surplus as milk than when they market milk products". What is more, milk is nutritionally of far greater value than *ghee*. It should not be overlooked that nearly half the milk production in India is converted into *ghee* so that, given the proper transport facilities, which are now lacking, the scope for raising the lamentable low per capita milk consumption through the existence of *Vanaspati* is appreciable (Appendix V).

But the contribution with which the public is most familiar is the marketing, for the first time in India, of fat in hygienic and convenient consumer packs, free from dirt and contamination which are still an inseparable feature of our bazars.

This, in brief, is what the *Vanaspati* Industry can legitimately claim to have done during its short existence. A word about what the *Vanaspati* Industry has not done seems, in the light of some popular misconceptions, to be necessary :

- (a) The *Vanaspati* Industry has not adversely affected the dairy industry and the agricultural economy of the country. Between 1940 and 1945, when the *Vanaspati* Industry witnessed its greatest development so far, the production of milk in India has not declined, on the contrary, it has risen by 5%. Nor has the price of *ghee* been unfavourably influenced by the increased availability of *Vanaspati*. Again, on the contrary, the price of *ghee* has registered a relatively higher increase - an increase of 86 points over and above the increase in the articles of food which make up the cost of living index (Appendix VI).
- (b) Nor has the *Vanaspati* Industry, as a result of the increasing demand for groundnut oil, deprived the poor man of his main source of fat. In point of fact, due to the reduction in the exports of groundnut seed and oil from an average of 3,50,000 tons, in terms of oil before the second world war to an average of less than 70,000 tons in terms of oil to-day, more oil is available to the consumer of groundnut oil in spite of the greater output of *Vanaspati* (Appendix VII).
- (c) The cost of hydrogenation is not high, indeed it is small. After the oil has been refined and deodorised it costs only about Rs. 15/- per ton to hydrogenate it. The difference in costs between crude groundnut oil and *Vanaspati* is about $3\frac{1}{2}$ annas per lb. Of this 1 anna goes to Government in the form of excise, $\frac{3}{4}$ anna goes for the cost of packing in tins and the rest goes largely to cover the cost of processing, including the oil loss.
- (d) The consumption of *Vanaspati* does not lead to blindness in the third generation. The premature publicity of the first incomplete experiment at Izatnagar - incidentally, later repudiated by the same Institute - may have brought the Institute prominently before the public and may have even given an air of immortality to some of its unfortunate rats; but I doubt very much whether it added to the Institute's reputation in the scientific world.

Before concluding I should like to make a reference to the problem of adulteration. Adulteration is undoubtedly a serious problem in India. A cynic once described adulteration as the largest

industry in the country. But it is a dangerous illusion to think that the adulteration of *ghee* is going to cease by eliminating *Vanaspati*. The adulteration of *ghee* will be brought within control only when the general problem of adulteration is tackled by the Government. What is more, there is no short-cut solution to it. India will have to do exactly what other countries have done, that is, to enforce the law and to create public opinion against the anti-social activities of the food adulterator. I confess, it is difficult for me to understand why so much feeling can be worked up against the small part *Vanaspati* plays in the adulteration of *ghee* when the adulteration of milk, drugs and medicines, for instance, is connived at or ignored. Finally, the idea of adding a colour to *Vanaspati* to render its adulteration with *ghee* impossible is another dangerous illusion. Nowhere in the world is this done; and no such colour is available. Nor will it solve the problem if it were done in India. The task of preventing adulteration, I would once again emphasise, rests entirely on the shoulders of the government.

I suggest that the time has now come to allow the *Vanaspati* industry to fulfil its functions unhindered by prejudice. Its need has been established and its contributions are of great value to the country.

APPENDIX I

Development of the *Vanaspati* Industry

Year	Number of Factories	Production (Tons)
1935	2	18,000
1938	5	38,000
1939	10	52,000
1940	10	62,200
1941	10	85,300
1942	12	77,300
1943	16	105,000
1944	17	117,200
1945	19	132,400
1946	22	145,000
1947	24	96,000
1948	27	130,000
1949	42	155,500
1950	42	171,415

APPENDIX II

Distribution of *Vanaspati* factories in various states

Sl. No.	State	In Production	Under construction.	Capacity Tons
1	Bombay ...	14	3	142,400
2	Saurashtra ...	3	1	22,500
3	West Bengal ...	6	1	53,000
4	Bihar ...	1	...	4,960
5	Orissa ...	1	...	7,500
6	Uttar Pradesh...	4	...	42,468
7	Delhi ...	2	...	13,500
8	Punjab ...	1	...	3,000
9	Pepsu ...	...	1	3,000
10	Madras ...	6	6	52,900
11	Mysore ...	3	...	7,800
12	Hyderabad ...	1	...	7,500
13	Travancore ...	1	...	1,200
14	Madhya Pradesh	2	...	19,500
15	Madhya Bharat.	1	1	10,500
Total ...		46	13	391,728

APPENDIX III

Productive capital invested in *Vanaspati* industry

Division	Rs.
East Punjab, Delhi, U.P. ...	2,38,89,345
West Bengal, Bihar, Orissa ...	4,11,47,431
Madhy Bharat, Madhya Pradesh & Hyderabad	3,00,51,217
Bombay, Saurashtra ...	9,52,13,920
Madras, Cochin, Mysore ...	3,42,47,302
Total in Rupees ...	22,45,49,215

APPENDIX IV

Contribution of *Vanaspati* Industry to the state exchequer

	1948	1949	1950
Production (Tons) ...	130,000	155,000	171,415
Income Tax Rs. ...	5333,000	2235,000*	2658,000
Excise „ ...	1,7224,000	2,1700,000	2,3800,000
Rly. Freight „ ...	9571,000	6594,000*	9655,000*
Sales Tax „ ...	8611,000	1,0850,000	1,1900,000
Town Duties, and Licence Fees etc, „ ...	2091,000	1560,000*	1658,000*
Total in Rs.	4,2830,000	4,2939,000	4,9671,000

*Incomplete.

APPENDIX V

(a) Annual production and utilisation of milk in the Indian union)

(In lakh maunds)

Total Milk Production	Fluid Milk	%	Ghee	%	Other Products	%	Total quantity converted into products Quantity	%
4,815.5	1740.96	36.2	2085.16	43.3	989.38	20.5	3074.54	63.8

(From "Report on the marketing of milk in the Indian Union, 1950")

(b) Comparative daily capita consumption of milk in India and in other countries in 1948.

Country	Per Capita Consumption oz.
India ...	1.8
Australia ...	14.0
Canada ...	19.0
Denmark ...	17.0
France ...	7.0
Holland ...	14.0
New Zealand ...	19.0
Norway ...	20.0
Sweden ...	22.0
United Kingdom ...	14.0
U. S. A. ...	17.0

APPENDIX VI

**Relative rise in price of *Ghee* and other articles of food
in cost of living index in Bombay state**

	Aug. 1939	July, 1951
Cost of Living Index ... (1934-100)	106	333
Price Index of <i>Ghee</i> ...	106	419
Price per lb. ...	(Rs. 0-12-11)	(Rs. 3-3-0)

APPENDIX VII

Availability of groundnut oil for home consumption

			In terms of oil - in tons	
			Pre-War	1950
Groundnut Oil Produced	...	...	672,000	692,000
Groundnut Oil Exported	...	...	344,000	68,000
Groundnut Oil used in Vanaspati	...		51,000	171,000
Groundnut Oil available for Home consumption	...	...	277,000	453,000

APPENDIX VIII

Specification for *Vanaspati*

1. It shall be prepared by hydrogenation from any edible harmless vegetable oils or mixture thereof except marine, mineral and animal oils. The prior approval of the Vegetable Oil Products Controller for India shall be obtained for admixture of more than 5 per cent. of any permissible oil in the product and the name of oil so used shall be clearly indicated on the containers.
2. It shall not contain any harmful colouring, flavouring or any other matter deleterious to health.
3. No colouring shall be added to it unless with the prior sanction of the Vegetable Oil Products Controller and in no event any colour resembling the colour of ghee.

4. If any flavour is used, it shall be distinct from that of ghee in accordance with a list of permissible flavours and in such quantities as may be prescribed by the Vegetable Oil Products Controller for India.
5. It shall not have moisture exceeding 0.25 per cent.
6. The melting point as estimated by the capillary slip method shall be from 33°C to 37°C both inclusive.
7. The Butyro Refractometer reading at 40°C shall not be less than 48.0.
8. It shall not have unsaponifiable matter exceeding 1.25 per cent.
9. It shall not have free fatty acids (calculated as oleic acid) exceeding 0.25 per cent.
10. The product on melting shall be clean and clear in appearance and shall be free from sediment and rancidity and pleasant to taste and smell.
11. It shall contain raw or refined sesame (til) oil not less than 5 per cent. by weight but sufficient so that when the vegetable oil product is mixed with refined groundnut oil in the proportion of 20:80 the red colour produced by the Baudouin test shall not be lighter than 2.0 Red units in 1 c.c. cell on a Lovibond scale.
12. It shall be manufactured in premises maintained under hygienic conditions.

APPENDIX XI

Conditions regulating the sale of *Vanaspati*

1. It shall not be sold from the same premises where ghee is sold.
2. Every dealer in *Vanaspati* shall display a sign board that *Vanaspati* is sold in his shop.
3. Every *Vanaspati* container shall be clearly marked in English and Hindi, in capital letters not less than $\frac{1}{2}$ inch high, with the words
 "Hydrogenated Groundnut Oil" or "Hydrogenated
 Coconut Oil" etc. as the case may be.
4. The names of all oils constituting more than 5% of the product shall be stated on the label.
5. The use of the word ghee to describe *Vanaspati* is prohibited.
6. The word *Vanaspati* should not be written on the containers in letters exceeding $\frac{1}{8}$ inch in height.

APPENDIX X

Consumption of butter (*Ghee*) and hydrogenated oil (Shortening, compound fats or *Vanaspati*)

1949 compared with pre-war in metric tons

Country	Butter		Hydrogenated Oil		% of Hydrogenated oil to butter	
	1949	pre-war	1949	pre-war	1949	pre-war
1 India ...	489,000	527,190 *	155,600	38,385 *	31.9	7.3
2 Pakistan ...	100,000	107,810 *	10,600	2,615 *	10.6	2.4
3 Argentine ...	37,000	30,000	7,800	21,000	21.1	70.0
4 Australia ...	90,800	102,600	31,300	20,800	34.5	20.2
5 Austria ...	20,000	22,000	26,600	19,700	133.0	89.6
6 Belgium ...	96,000	66,200	64,400	62,900	67.1	95.0
7 Brazil ...	31,000	24,000	21,000	5,900	67.7	24.0
8 Burma ...	10,000	10,000	30	950	0.3	9.5
9 Canada ...	148,700	156,400	62,650	53,500	42.1	34.2
10 Ceylon ...	850	500	1,600	500	188.2	—
11 Denmark ...	16,000	31,350	49,100	85,000	306.9	217.1
12 Finland ...	36,400	36,000	14,650	15,000	40.2	44.2
13 France ...	217,000	215,000	76,000	70,000	35.0	32.5
14 Germany ...	239,300	589,000	295,000	468,000	123.2	79.4
15 Holland ...	32,400	47,400	173,400	84,800	535.2	178.9
16 Indonesia ...	300	4,700	12,100	3,150	4033.3	67.0
17 Ireland (Eire) ...	58,700	43,900	6,300	5,400	10.7	12.3
18 Israel ...	825	3,250	7,300	1,600	884.8	49.2
19 Italy ...	45,000	50,000	20,000	10,000	44.4	20.0
20 Malaya ...	1,250	1,820	1,150	1,300	92.0	71.4
21 New Zealand ...	27,400	30,000	8,750	3,000	31.9	10.0
22 Norway ...	18,700	16,700	69,500	57,900	371.6	346.7
23 Philippine Isles ...	950	750	22,000	13,700	2315.8	1826.7
24 South Africa ...	30,000	30,900	13,200	4,400	44.0	14.2
25 Sweden ...	99,500	71,500	71,800	64,700	72.2	90.5
26 Switzerland ...	24,000	29,900	31,000	19,000	129.2	63.5
27 United Kingdom ...	310,300	529,800	624,300	276,900	201.2	52.2
28 United States ...	704,400	989,300	1034,200	798,800	146.8	80.7

*Adjusted

*Adjusted

THE NUTRITIVE VALUE OF VANASPATI

BY

DR. M. DAMODARAN

National Chemical Laboratory, Poona.

The function of fat in the dietary is to serve as a source of energy. Weight for weight the calorific value of fat is twice that of proteins or carbohydrate and it is, therefore, superior in this respect to the other constituents of diet. The intake of fat is, however, limited by the fact that its proper utilization in the body requires the simultaneous ingestion of adequate amounts of carbohydrate and protein. When the proportion of fat to carbohydrate is excessive there is incomplete combustion of the former with the formation of toxic products, the ketone bodies. In the absence of sufficient amounts of protein, in particular of certain amino acid constituents, such as methionine, derived from protein there is infiltration of fat into the liver ending in the long run in hepatic cirrhosis. So important is the balance between fat and the other primary constituents of the diet that in certain species, such as the rabbit, administration of even small amounts of fat produces fatal results. In the human dietary the correct proportion of fat is considered to be an amount which contributes about 25 per cent of the total calories.

The relative nutritive value of dietary fats does not constitute an important nutritional problem, most edible fats having been shown by experiment to be equally well utilized, as can be seen from Tables I, II & III showing the digestibility, absorption and rate of growth obtained with different fats.

TABLE I
Digestibility of various oils and fats

Fat used in the test	Digestibility	
	I ¹	II ²
Butter fat (cow)	99.2	99.7
Butter fat (buffalo)	98.8	—
Sesame oil	96.0	98.0
Mustard oil	95.5	95.8
Coconut oil	98.4	97.9
Hydrogenated coconut oil	98.5	—
Groundnut oil	99.7	98.3
Hydrogenated groundnut oil m.p.37°C	99.5	98.1
Hydrogenated groundnut oil m.p.39°C	—	95.9
Hydrogenated groundnut oil m.p.43°C	—	96.5
Cotton seed oil	—	97.6
Hydrogenated cotton seed oil m.p.35°C	—	96.8

TABLE II

Percentage absorption of fats by human subjects³

Name of fat	No. of observations	Percentage absorption of added fat		
		Lowest	Highest	Average
Groundnut oil Crude ...	20	91.16	97.32	94.97
Groundnut oil Refined ...	21	91.62	99.20	96.03
<i>Vanaspatti</i> -m.p. 37°C ...	10	89.88	95.60	93.63
<i>Vanaspatti</i> -m.p. 41°C ...	9	86.22	93.23	90.04
<i>Ghee</i> ...	11	90.14	96.64	93.74

TABLE III

Effect of fats on rate of growth⁴

Fat	% Composition of Diet			Mean daily gain in wt. g./rat	Average daily food in take g.
	Fat free basal diet*	Vit. B complex Solution	Fat		
I. Butter fat ...	80	10	10	4.28	17.2
II. Oleomargarine (hydrogenated Cottonseed oil) ..	80	10	10	4.27	17.3
III. Olive oil ...	80	10	10	3.99	16.4
IV. Cottonseed oil...	80	10	10	4.42	19.7
V. Fat free diet ...	90	10	—	3.63	20.2

* Fat free basal diet consisted of :—

Vitamin free casein	...	30.0%
Sure's Salt No. 1	...	4.5%
Sucrose	...	65.2%
Cystine C. P.	...	0.3%
2-methyl, 1:4 naphthaquinone		1 µg/g

It is generally accepted that there is no appreciable difference in the nutritional value of fats whose melting points do not greatly exceed body temperature. Even the practical importance of this criterion is doubtful as high melting fats are readily absorbed when admixed with fats of lower melting points.

Hydrogenated oils have presented no exception to the general behaviour of edible fats in the matter of digestibility, absorption or utilization for growth; this will be obvious from the figures for such fats in the above tables. The first patent for margarine was taken out in France in 1869, and hydrogenated oils have been widely used in human dietaries for generations without any deleterious effect on health.

The objection raised by certain sections of the public in India to the use of hydrogenated oils (*Vanaspati*) is stated to be based on experiments according to which the feeding of *Vanaspati* to rats in successive generations led to night blindness, loss of fertility and other deficiency diseases. These experiments were, however, carried out with a diet so thoroughly unbalanced that they were bound to give the observed results, irrespective of the nature of the fat included in the diet. In attempting to repeat these experiments it was found by several authors, as was to be expected from the known influence of fat on unbalanced diets, that a second generation of animals could not be obtained on the diet originally used. With properly controlled experiments, it was found in several laboratories that hydrogenated oils showed none of the alleged deleterious effects. Results in Table II are typical of those obtained. There is no doubt that the alleged deleterious effects obtained as a result of feeding hydrogenated oils was due to the unbalanced nature of the diets used, and had no bearing on the specific nature of the dietary fats. The harmful effect of unbalanced amount of fat in low protein diets is illustrated in the Table IV.

From these results which are in agreement with previous findings of other authors the following conclusions may be drawn:—

- (i) that the butter fat or *ghee* incorporated in low protein diet is more harmful than coconut, sesame or mustard oil and
- (ii) that evaluation of the nutritive value of fats by experiments in which they are incorporated in otherwise unbalanced diets is without practical significance.

While most edible fats differ little from each other as source of energy, the vegetable fats including the hydrogenated products derived from them are inferior in one important respect to certain animal fats such as butter fat, cod liver and other liver oils, in that the latter contain vitamins A and D. If, therefore, *Vanaspati* is to be used as substitute for butter or *ghee* it is necessary that the product should be fortified by the addition of necessary vitamins. Industry has already accomplished this for margarine, preparations of which are obtainable with vitamin contents superior to that of natural butter. Similar

TABLE IV

Effect of dietary fat on growth and liver fat content⁵

Diet	No. of animals	Food intake (g/day)	Initial body wt. (g)	change in body weight* %	LIVER		
					body wt. %	Crude fatty acids	
						Fresh weight %	mg/100g. rat
Protein - 20%	6	8.0	76.5	40.0 ± 3.7	3.45	4.47 ± 0.22	155
Protein - 5%, Coconut oil - 15% ...	6	6.0	79.0	14.6 ± 3.9	5.00	9.06 ± 1.43	447
Protein - 5%, Coconut oil - 25% ...	6	5.5	68.5	6.7 ± 3.2	5.03	8.84 ± 0.99	439
Protein - 5%, Ghee - 15% ...	6	5.3	85.3	2.3 ± 3.2	3.86	7.03 ± 0.50	273
Protein - 5%, Ghee - 25% ...	6	5.4	87.6	-0.9 ± 3.1	4.17	7.02 ± 0.57	332
Protein - 5%, Sesame oil - 15% ...	7	5.4	87.4	10.1 ± 2.0	3.89	4.37 ± 0.19	173
Protein - 5%, Mustard oil - 15% ...	6	5.0	81.3	5.3 ± 3.8	3.70	4.21 ± 0.22	156

* Group means with their standard errors.

fortification of *vanaspati* with vitamins should be the aim of the Indian hydrogenated oil industry, as there is not the remotest possibility that the vitamin A requirements of our population will be met by milk or butter. The fact that both vitamins A & D are now manufactured by synthetic processes from raw materials available in India makes this a realizable objective.

References :

1. Roy, A., *Annals of Biochemistry & Experimental Medicine*, 1944, **4**, 17.
2. Langworthy, C. F., *Industrial & Engineering Chemistry*, 1923, **15**, 276.
3. Bose, S. M. and Subrahmanyam, V. – Unpublished data.
4. Lassen, S. and Bacon, E. K., *J. Nutrition*, 1949, **39**, 83.
5. Damodaran, M. and SivaRaman, C., *Ind. Jour. Med. Res.* 1951, **39**, 465.

DISCUSSION

Dr. N. N. Godbole raised the objection on feeding experiments on rats for finding out the nutritive value of *vanaspati*, because there would be a fundamental difference between the diet of a man and a rat. Moreover, the digestive organs of a rat might be functioning differently than those of human beings. In his opinion the melting point of a fat should be the main deciding point of the value of the fat as human food. He regarded that the Baudouin test for sesamol as the best for the detection of *vanaspati*, and no other colour need be added. If they decide colouring *vanaspati* with any other colour, many questions as to its amount, effect on dilution with other fat and its action on the human body after taking such coloured *vanaspati* for a long time would arise.

Mr. D. K. Gupta pointed out that by hydrogenation the unsaturated acids of the fat which are very essential for human nutrition were being decreased. *Ghee* has certain fatty acids which are necessary for human nutrition and therefore, it cannot be substituted in human diet by *vanaspati*. He was also of the opinion that *vanaspati* factories were wasting lot of oil in its preparation.

Dr. R. K. Trivedi of Bombay remarked that oils could not advantageously be used in all types of processing of food. In frying, hydrogenated oil would be superior to other oils on account of its higher cracking temperature.

Mr. Shohet pointed out that oils could not be kept for a long time because they become rancid quickly while *vanaspati* could be kept for a very long period in a good palatable condition. According to the Government specifications, the melting point of *vanaspati* should not be more than the human body temperature. In his opinion also colouring of *vanaspati* would not solve the problem of adulteration and some more severe actions by the Government would be necessary. He further informed that only 5 per cent of the oil was wasted in the manufacture of *vanaspati*.

Dr. Damodaran referring to Dr. Godbole's objection of feeding experiments on rats pointed out that all the medical and physiological knowledge especially on nutrition is based almost entirely on the results obtained on animals such as rats, guinea-pigs and dogs. Regarding the nutritive value of unsaturated acids, Dr. Damodaran informed that nobody had been able to verify that fats containing acids having 2 or 3 double bonds were absolutely essential for human nutrition. He suggested that it would be much better if hydrogenated oils could be vitaminised.

Mr. Shohet informed that attempts in that direction were being made.

Mr. T. V. Subbarao of Tata oil Mills said that the amount of linoleic acid required by a human being is very small and could be obtained from oils present in other food materials as rice and wheat. Moreover, the presence of 5 percent sesame oil that had to be added to *vanaspati* would give much more linoleic acid than required by the human body.

Dr. Saletore suggested the necessity of comparative experiments on various types of Indian cooking with *vanaspati* and other edible oils. He further pointed out that margarine in many respects compared very favourably to butter, yet *vanaspati*, as it was being produced was not as good as *ghee* in many respects such as flavour, taste, appearance etc. In his opinion the future of *vanaspati* lay in removing such drawbacks.

A STUDY OF CATALYST IN VANASPATI PRODUCTION

BY

D. D. NANAVATI

Palanpur Vegetable Products Ltd., Palanpur (N. Gujerat).

Fats are used chiefly as food and hydrogenated groundnut oil (*Vanaspati*) is one of the common cooking medium for Indian people. The progress of hydrogenation technology in India has opened up fresh avenues for the utilization of fats and their conservation. Besides the key industry of the *Vanaspati*, a number of side industries also have expanded such as soap industry, oil crushing, glycerine recovery etc. All these products have augmented the importance of hydrogenation industry. Today, the chief use of hydrogenation industry is the fact that it supplies product similar to genuine *ghee*.

The catalyst commands an important place in the technology of *Vanaspati* industry. Though there are a number of patented processes in use which may or may not provide good results, many establishments still reduce nickel formate in autoclave type reducers despite the advantages of more upto-date electrically controlled automatic devices. Catalyst reduction plays a very important part in the *Vanaspati* industry. The degree of hydrogenation and characteristics of texture and grains in *vanaspati* largely depends upon the quality of nickel produced. It is determined largely by the following factors:—1. quantity of nickel formate, 2. method of reduction, 3. quantity and quality of base selected, and 4. design of reducer. The cost of reduction and the technical difficulties will be reduced in direct proportion to the simplicity of the 'reduction' procedure.

Reduction Processes :

It is the term applied to the treatment of nickel formate with heat under the atmosphere of hydrogen. In general, the industry refers to this process as a recovery or disintegration. The methods used or proposed for the commercial preparation of hydrogenation catalysts from the oxide, hydroxide, and formate of nickel does not differ in principle from each other. The following is offered, therefore, as a rough division of the various methods according to their features.

1. Straight reduction in hydrogen.
2. Reduction in two stages, first at 200°-300°C. and 760 mm and second, at the same temperature and at 4-5 atmosphere pressure.
3. Surface reduction.
5. Reduction in various liquid media or melted media such as paraffin wax, vaseline, fat and naphthalene.

Reduction in liquid media.

It is by far the most important process that is followed today in our country. Reduction in liquid media refers to any method of treatment of nickel formate with heat under atmosphere of hydrogen and in the presence of refined and bleached vegetable oil. Because of convenience, wet reduction process is extensively used for preparing the catalyst. Although other organic salts of nickel are available, still the formate is in vogue because it is not only easily prepared but also leaves no organic residue on reduction.

To prepare the catalyst, well ground nickel formate is heated in oil at 240° to 250°C and hydrogen is passed through. In five to six hours, catalyst is obtained.

A part of the nickel formed by the decomposition of nickel formate possesses colloidal properties. The problem of filtration is not, however, a serious one, as it has been found that by the addition of a filtration agent such as hyflo; the nickel is retained satisfactorily in the filter press.

Three different methods of reduction were tried by the writer.

Design of the equipment used for the above experiments.

A cylindrical reducer of 2' diameter and 5' high with a jacket in the bottom was used for these experiments. It had a small propeller in the bottom side with a perforated hydrogen coil inside. There was no vacuum equipment provided with the system, hence inert atmosphere had to be maintained from the time heating started. The reducer could hold a maximum of 240 lbs. of refined and bleached G. N. oil with an average 40 lbs. of nickel formate. With the above equipment three different experiments were carried out, the details of which are given below :—

1st EXPERIMENT

Charge :

- (1) 40 lbs. of nickel formate.
- (3) 160 lbs. of R. & B. G. N. oil.
- (3) No base was used.
- (4) Final temperature of reduction was set at 450°F.

Process :

The temperature of the reducer was allowed to rise as rapidly as possible until it reached about 365°F. When the temperature had reached about 302°F., the initial reaction began. The reaction being exothermal very little hydrogen was passed to facilitate the escape of the gaseous fumes emitted during the evolution of steam from the water of crystallisation of nickel formate. The temperature was maintained at 375°F; until the preliminary activity in the reduction was over, and the moisture driven off. The temperature was then raised quite rapidly to 450°F when nickel formate was converted into nickel. When the reaction was complete which was judged by the colour of the catalyst and m. p. of the stearin produced, the heating elements were switched off, the charge was allowed to cool slowly by itself under the influence of cold hydrogen circulation; water was not used in the jacket for cooling the catalyst.

Observation :

- (1) the time required to complete one batch was 8 hours.
- (2) Total amount of hydrogen required from beginning to end of the process : 4000 cu. ft.
- (3) Quality of nickel obtained :—It was jet black in colour and highly colloidal in texture. It gave a red filtrate when filtered through a bed of hyflo. It hydrogenated the oil from medium to stearin with a melting point of 60°C the hardening properties of nickel thus reduced were finally studied in the convertor. The following observation were recorded.

Hydrogenation :

- (1) The proportion of the mixture was 1 to 0.12 per cent by wt. of oil to nickel.
- (2) Hydrogenation pressure in the convertor was maintained at 25 lbs.
- (3) Exothermic temperature of hydrogenation was allowed to rise upto 400°F.
- (4) 2½ tons of R & B groundnut oil took 30 minuts to consume 2062 cu. ft. of hydrogen to give hydrogenated oil of 38°C melting point.
- (5) The hydrogenated GN oil was then analysed for I.V. 2062 cu. ft. of hydrogen gave a drop of 37 I.V. from 92 to 65.

Though the rate of hydrogenation was quite satisfactory the catalyst was not selective. We observed that a drop of only 27 I. V. was obtained for M.P. of 38°C and with a very low consumption of

hydrogen. The setting characteristics of vegetable product were studied in a refrigerator. It was observed that the product was very soft in texture and did not grain properly. The product after filling into the tins separated into two layers in the cold room. The product gave pseudo M.P. and it did not correspond with its I.V., the reaction was not selective. Owing to its non-selectivity, it could not suit our requirements.

2nd EXPERIMENT

Charge :

- (1) 40 lbs. of nickel formate.
- (2) 160 lbs. of R & B groundnut oil.
- (3) No base was used.
- (4) Final temperature of reduction was set at 485°F.

Process :

In the initial stage the same process was followed as in the case of the 1st experiment. The final temperature was, however, raised to 475°F instead of 450°F as was done in the previous experiment. When the reaction was complete, the batch was cooled by circulating cooled water in the jacket.

Observation :

- (1) Time required to complete on batch was 6 hours.
- (2) Total amount of hydrogen required for the complete batch.....3000 cu. ft.
- (3) Nickel obtained was jet black in colour and highly colloidal in texture. It gave a pink filtrate when catalyst was filtered through a bed of hyflo. It hydrogenated the oil from medium to stearin with a melting point of 57°C. The hardening properties of nickel thus obtained were studied in the convertor.

Hydrogenation :

The conditions of hydrogenation were the same as in the first experiment. The following observations were recorded.

- (1) The nickel was highly colloidal and the filtrate of hydrogenated oil was deep red in colour.
- (2) The colloidal nickel was not arrested by hyflo. It was observed that colloidal nickel acted as an emulsifying agent and formed insoluble nickel soap with hardened oil when refined. It gave a lot of trouble in refining of crude hard oil, appreciable quantity of catalyst was lost in the filtrate of hardened oil and became

gelatinous very rapidly. This catalyst did not hydrogenate more than 20 batches of oil i.e. 50 tons of G. N. oil successfully, it became gelatinous and refused to filter through a thick coating of hyflo. Though it had become gelatinous, it did not lose both its activity and selectivity. It was highly selective and gave a product of 62 I. V. for the consumption of 1100 cu.ft. of hydrogen per ton of oil. The rate of consumption of hydrogen was the same as in the 1st experiment and the product gave very good texture with bold grains when set into tins. To save the catalyst from becoming gelatinous, the third experiment was tried in the same equipment.

3rd EXPERIMENT

Charge :

- (1) 40 lbs. of nickel formate.
- (2) 160 lbs. of F. & B.G.N. oil.
- (3) 4 lbs. of hyflo as a base for nickel was used.
- (4) Final temperature of reduction was set at 475°F.

Process :

The same process was followed as in the case of 1st experiment in the initial stage of the process. The primary reaction was over within half an hour at 374°F. The temperature was then rapidly raised to 475°F. and maintained for 1 hour. When the reaction was completed the batch was cooled by circulating cold water in the Jacket.

Observation :

1. Time required to complete one batch - 8 hours.
2. Total amount of hydrogen required for the complete batch of reducer - 3000 cu.ft.
3. Quality of nickel obtained was jet black in colour and granular in texture. It gave a clear filtrate when catalyst was filtered through a bed of hyflo. It hydrogenated the oil from medium to stearin (m.p. 37°C). The hardening properties of nickel thus obtained were studied in the convertor.

Hydrogenation :

The conditions of hydrogenation were the same as in the first experiment. The following observations were recorded :

- (1) The nickel was granular and the filtrate was very clear.
 - (2) The granular nickel was immediately arrested by hyflo.
- There was no difficulty in refining of hardened groundnut oil. It formed very little emulsion and the final product was very good in colour and texture.

(3) It gave a drop of 32 I.V. from 82 to 60 for a product of 38°C melting point and for a consumption of 1100 cu.ft. hydrogen per ton.

The above catalyst did not become gelatinous until it become inactive and 13 lbs. of nickel hardened 125 tons of groundnut oil which works out to one pound of nickel for hydrogenating 10 tons of G. N. oil.

Conclusion :

Subsequently a few more experiments were tried to see whether any more improvement could be made in the quality of catalyst. But it was observed that the best nickel, selective in nature, is prepared by reducing the formate at 475°F. for 1 hour. The mixture of oil and nickel formate should be in the proportion of 1 to 4 to avoid frothing in the reducer.

It is obvious that the composition of a partially hydrogenated oil can be regulated to some extent by controlling the conditions of hydrogenation in the case of vegetable shortening. It is also important not to harden the product above the desired m.p. but at the same time to reduce the linoleic acid to minimum to achieve granular texture. The extent to which the reaction is thus selective with regard to linoleic acid is determined chiefly by: quality of catalyst, pressure of hydrogenation, temperature of hydrogenation, and concentration of catalyst.

HIGH PRESSURE TECHNIQUE FOR FAT SPLITTING AND HYDROGENATION OF FATTY ACIDS

BY

DR. R. K. TRIVEDI

Industrial Chemist, Bombay.

Free fatty acids have been known to be produced by various methods, but the application of high pressure technique with a view to obtain free fatty acids and pure glycerine should prove of great interest to the oil industry. When we consider the problems facing the manufacture of soap by saponification methods, as also the difficulties experienced in the refining of glycerine; the introduction of high pressure technique in the splitting of vegetable oils and fats would certainly be a great step forward in the right direction towards the solution of this problem.

The production of free fatty acids by the utilisation of Indian oils would also open up possibilities of producing higher fatty alcohols by the high pressure hydrogenation of these acids. It is, therefore, proposed herein to treat in merest outlines, the high pressure technique in fat splitting and hydrogenation of fatty acids.

Technical Considerations :

The process for fat splitting at high pressure depends upon a very simple principle. The equipment is simple in design and consists of :—

1. High pressure feed pump for feeding the autoclave with preliminary supply of water and later on with oil or a suitable fat.
2. High pressure fat splitting autoclave operating at working pressure of 455 lbs/sq. inch.
3. A detention vessel for discharging the autoclave after the completion of the wetting process.
4. A tubular condenser for condensation of vapours originating from the detention of the autoclave contents.
5. A decanting equipment to separate the glycerinous liquor and free fatty acids.
6. Tanks for receiving the free fatty acids.

The process depends upon the application of high pressure to a mixture of water and raw vegetable fat in the autoclave under a working pressure of 455 lbs. per sq. inch at the corresponding temperature of 230°C. The duration of the splitting process proper will be 2 to 3 hours. No addition of any chemicals or splitting reagents is necessary to accelerate the splitting of the oil. This fact permits considerable economy. On the other hand the glycerine water obtained from the splitting will not necessitate any elaborate processing as there are no foreign reagents. The two main products are the free fatty acids and glycerin liquor.

For obtaining the best results, a determined quantity of water is fed by the high pressure pump into the autoclave. While this is being done the autoclave is maintained under reduced pressure. The next step is the feeding of the raw fat to the autoclave. Steam is slowly admitted until process temperature and pressure are reached. After the splitting is completed the contents of the autoclave are discharged to the detention vessel. The quantity of condensed water can be reutilised for splitting process.

The fat splitting process described above would operate on the following basis :—

1. No chemicals required whatsoever.
2. Splitting efficiency 95 per cent.
3. Steam consumption for all purposes will be 500 kg. per ton of the vegetable oil.
4. Power consumption per ton of raw oil is 15 kwh.
5. Cooling water losses : 3 cu. meteres.

High pressure equipment should include a high pressure boiler operating at 500 lbs. per sq. inch pressure.

A small plant to produce about 1 ton of fatty acids would cost about Rs. 1,00,000/- including the high pressure boiler.

The cost of raw fatty acids in the form of cakes works out to about 4 to 5 annas per lb. The glycerine could be recovered by means of an auxiliary plant costing about Rs. 80,000/- for the corresponding capacity.

High pressure hydrogenation of fatty acids :

The fatty acids produced by the high pressure technique could be sold directly to the consuming industries or could be further treated to produce higher fatty alcohols by high pressure hydrogenation method.

The equipment consists of five units:-

1. High pressure hydrogenation plant.
2. Hydrogenation compressing and intermediate storage group.
3. Wash and storage plant for low pressure.
4. Electrolytic cell house to produce pure hydrogen.
5. Unit for preparing the catalyst.

The temperature must be 250–350°C and the hydrogen pressure approximately 300 atm. in order to obtain the corresponding alcohol. Double bonds in the raw material can be hydrogenated at the same time that the reduction of the carboxylic group takes place. It is also possible to keep the double bonds intact; the special catalyst used for the synthesis of fatty alcohols shows selective hydrogenation activity. The temperature in the autoclave should remain under 350°C. to avoid hydrocarbon formation. The quality of the fatty alcohols thus produced depends on the composition of the raw material :

- (a) free fatty acids containing saturated and unsaturated fatty acids can be transformed into saturated fatty alcohols;
- (b) glycerides containing saturated and unsaturated fatty acids are split and simultaneously reduced with the production of saturated alcohols, while glycerine is also reduced to isopropyl alcohol,
- (c) unsaturated fatty alcohols can also be produced after esterifying the unsaturated fatty acids with volatile aliphatic monoalcohols which in turn are recuperated.

The available raw materials, such as fatty acids or products obtained by esterification of free fatty acids or natural glycerides, are mixed with a special catalyst and injected by means of a feeding pump through a preheater into the autoclave in which the hydrogen circulates continuously at a pressure of about 250 atm. As soon as the reaction is completed, as can be observed by the amount of hydrogen absorption, the content of the autoclave is discharged through a cooler into another autoclave and then filtered in order to separate the catalyst. The hydrogen while circulating carries out of the autoclave the water formed during the reaction and also the lighter alcohols which are condensed in a third separate autoclave. The percentage of light alcohols separated by the hydrogen, in comparison with the heavy alcohols which are discharged from the reaction autoclave, can be controlled at will. Usually the light alcohols are 10–15 percent of the heavy alcohols. The hydrogen absorbed during the reaction is replaced in the system from high pressure cylinders

kept at the desired pressure, by means of a compressor. The hydroxyl value is practically a theoretical one; in the case of coconut oil it is about 270-280.

Consumption figures for the productions of 1 ton of fatty alcohols:

Fatty material	... 1150 - 1250 kg. (2500 - 2750 lbs.)
Hydrogen	... 250 - 500 Cu. meters (9000 - 18000 cu-ft).
Catalyst	... 20 - 50 kg. (44 - 110 lbs.)
Cooling water (15°C)	... 240 cu. meters (8000 cu.ft.)
Steam at 1.5 atm. (21 lbs./sq. in.)	... 1200 kg. (2600 lbs.)
Steam at 5 atm. (70 lbs./sq.in) ...	
(only if esterification of fatty acids is required)	... 1800 kg. (3960 lbs.)
Power (not including electrolyser).	2000 kWh.
Labour	... 3 workmen/shift.
Efficiency of the hydrogenation	
Process	... 96% $\pm$ 2% of the theoretical efficiency.

Characteristics of the fatty alcohols manufactured.

Saturated alcohols :

Acid value : 0 - 0.2 ; Saponification value : 2 - 8 ; Iodine value : 0 - 3 ; Colour : Colourless.

Un-saturated alcohols :

Acid value : 0 - 0.2 ; Saponification value : 6 - 10 ; Iodine value : More than 50 ; Colour : Light yellow.

The production unit complete with five auxiliary plants mentioned above with a capacity of 1 ton of higher fatty alcohols such as lauryl alcohol would cost Rs. 10,00,000/-.

FISH OILS

SHARK LIVER OIL INDUSTRY IN INDIA

BY

S. M. ARSIWALA

Department of Fisheries, Bombay.

The nutritive properties of fish liver oils have been known for centuries and they were being used for the treatment of rickets, night blindness and other deficiency diseases in the middle ages. The discovery that they contain the Vitamins A and D has given a scientific basis for the early belief. This discovery also led to the idea that different varieties of fish livers might also yield these vitamins. Investigations of fish liver oils have been continuously carried out during the past quarter of a century with the result that vitamin rich oils and concentrates are now prepared from a variety of fish livers.

During the initial stages of vitamin research cod liver oil was thought to be a rich source of vitamin A and D. But it was not long before other richer sources of these vitamins were discovered. It was soon found out that Halibut liver oil and shark liver oil were much superior sources. The average vitamin A potency of cod liver oil is about 1,000 I.Us/Gm. and it hardly exceeds 3,000 I.Us/Gm. Halibut liver oil, on the other hand, contains on an average 50,000 I.Us/Gm., the maximum being as high as 300,000 I.Us/Gm. The vitamin 'A' potency of shark liver oil averages 15,000 I.Us/Gm., which sometimes reaches as high as 200,000 I.Us/Gm.

The Nazi conquest of Norway during the world war II, cut off supplies of cod liver oil to the world. Alternative sources of vitamins A and D were intensely sought for in all parts of the world and soon shark liver oil was produced in U.S.A., Canada, Australia, New Zealand, South Africa and India.

In India, the pioneers in this industry were the Governments of Bombay and Madras, who have factories for the production of shark liver oil. During the years of war, they supplied fully the needs of the armed forces and now meet the demand of the civilian population. Thus, what was meant to be a stop-gap enterprise to tide over difficulties created by the war has now turned out to be one of the permanent major industries of the fish trade. The manufacture of shark liver oil at Bombay and Madras is now done on a commercial scale. The Bombay factory is not only in a position to meet internal

demands, but it has also been able to export 5685 gallons of shark liver oil worth Rs. 1,30,731/- to the U.S.A., the U.K., Australia and Iceland during the last three years.

At Bombay and Madras, the oil is extracted from the fatty livers of sharks which belong to the group of cartilaginous fishes which include the skates, rays and dog fishes. There are about 69 species and 57 of them are represented in our waters. Of these only 20 species are of commercial importance.

Sharks have no bony skeleton to support the body. They are of various sizes. A few even attain a length of 40 feet. They are most numerous in seas and estuaries of tropical regions.

Sharks occur at different depths, from surface to deep down as low as 1000 fathoms: from shallow waters round the coast to mid-oceans. Predacious as they are, their food is highly diversified, ranging from plankton, molluscs, crustaceans, vertebrates or even other fishes of no small size. In addition, the bigger sharks sweep at anything that comes in their way and unusual articles such as biscuit tins, sheep, whole bags of rice and at times human skulls and bones have been found as stomach contents.

Method of fishing:

Sharks are mostly caught by the line and hook method. Bigger hooks are used in case of large sharks. Bag nets and drift nets are other methods adopted in catching sharks.

Size of Shark Livers:

Livers of sharks vary in size depending upon the size of the shark. A single liver may be anywhere from a few ounces to 500 lb. in weight. The liver oil content varies from season to season and from shark to shark depending on several other factors. Wide variations are also observed in the vitamin 'A' potency of the oils. These have been found to be affected by such factors as fishing grounds, size, sex and spawning period.

The method of extraction:

Various methods for extraction of oil from the livers are followed. These are - steaming of livers, alkali digestion method, enzyme and alkali digestion process, solvent extraction method. The generally accepted method is, however, steaming process. Fish livers are freed from gall bladders, washed and finely disintegrated. Low pressure steam is piped in a tank containing the livers. The heat of the steam cooks the livers. The steam condenses and forms a layer of hot water upon which the oil floats. The oil is then either dipped off, or the tank is fitted with an overflow. The oil is transferred into a settling tank and washed with cold water to remove the

liver debris. The clear oil is further treated with anhydrous sodium sulphate to remove the last traces of water in the oil or dried in vacuum. Finally the oil is filtered through a filter press and stored in containers in an atmosphere of nitrogen.

The samples of oil extracted are assayed for vitamin 'A' content spectrophotometrically and analysed for F. F. A., unsaponifiable matter, iodine and other values.

Concentration of vitamin 'A':

Many patents covering the process for the concentration of vitamin 'A' in fish liver oils have been issued. These comprise descriptions of techniques and physical and chemical methods for separating the unsaponifiable matter in which the concentrate is found. The process in general and as followed by the Haffkine Institute, Bombay, consists of splitting the triglycerides into glycerol and fatty acid, which are then combined into soaps. Unsaponifiable material containing Vitamin 'A' is separated by means of solvents. One of the factors in the treatment of liver oils by this method is the percentage of unsaponifiable material contained in the oil. An oil having a high percentage of unsaponifiable material and a low vitamin 'A' potency cannot be converted into a concentrate by this method. According to the U. S. P. definition, a concentrate is one in which the potency of Vitamin 'A' is 200,000 I.U.s/Gm. or more. Oil from some species of sharks cannot be concentrated above 50,000 units because of the high unsaponifiable fraction in it.

The capsulating process :

Vitamin 'A' concentrates are more easily handled if they are in capsule form. If these concentrates are sold in liquid form in dark coloured glass bottles for home use, the loss of vitamin potency through oxidation is considerable after the bottle is opened. The pharmaceutical houses have found that the most satisfactory method of distributing the concentrates is in a single dose in the form of an easily swallowable capsules. With the capsule it is possible to include other vitamins in additions to 'A' which results in a single capsule containing multiple vitamins and of various predetermined potencies. All vitamin concentrates are carefully assayed before being capsuled.

The Government of Bombay have already imported one capsule making plant from the U. S. A., which is installed at the Fisheries Technological Laboratory at Bombay and will soon go into production.

Vitamins for live stocks:

Vitamins A and D are not only needed by human beings, but are equally important in the dietary of livestock. In most western countries, farm animals consume as much liver oil as human

beings. In Canada for instance, about 100,000 gallons of liver oils are administered to farm animals. It is natural to expect that shark liver oil will play no small part in the improvement of our livestock in which so keen an interest is now being taken on all sides.

Industrial use of shark liver oil :

Shark liver oil with low Vitamin 'A' content or which is unfit for medicinal purposes because of the high F. F. A. and disagreeable odour is sold as industrial shark liver oil and is used by many industries.

Industrial shark liver oil is used in the leather tanning industry. As a currying oil it softens and lubricates the leathere fibres. It is also used in the manufacture of paints, varnish, printing inks, oil cloth and linoleum. The steel industry uses it for tempering springs and other articles, made of steel.

Livers of sharks are not only used for the extraction of oil, but are also found to be very rich in anti-anaemic factors. Recently the process of manufacture of fish liver injectibles is patented by Bhatavdekar and Shirsat. Clinical trials have shown that the fish liver extract is more beneficial than sheep or pig liver extracts.

Thus the livers of sharks have become economically more important to fishermen than the whole shark.

DISCUSSION

In the opinion of **Mr. Om Prakash**, non-edible oils should be used for various industrial purposes. One of the sources of such oils is the oil seeds. The other source should be fish oils. He wanted to know from **Mr. Arsiwala** whether Government was taking necessary action to exploit the fish oil for those purposes.

Dr. J. S. Aggarwal also wanted to know from **Mr. Arsiwala** whether besides sharks other fishes were also available near the sea-coasts of India and what was the price of industrial shark liver oil.

Mr. Arsiwala informed that at that time the Government had been taking precautions to step up the production of shark liver oil. But the position had become quite difficult due to the synthetic vitamin 'A' coming in the market from America and it was available at a much cheaper rate. Therefore, they had to pay less price for shark livers which created dissatisfaction among the fishermen. Further, there were fishes in Indian waters from which the body oil could be exploited. He also informed that the price of industrial shark liver oil was about Rs. 6/- per gallon but quantity was very small and at present this amount could not be increased as they were trying to produce as much improved quality of oil as possible.

CASTOR OIL, DRYING OILS,
PAINTS AND VARNISHES

SOME INVESTIGATIONS ON HYDROXY OILS PARTICULARLY CASTOR

BY

DR. K. T. ACHAYA & DR. S. A. SALETORÉ

*Central Laboratories for Scientific and Industrial Research,
Hyderabad (Deccan).*

Results of our investigations on hydroxy oils, particularly castor, are discussed in this paper.

The evaluation of castor oil and hydroxy acids using the refractive index:

During our studies on castor oil, we happened to find that acetylation lowered the refractive index considerably, by 0.0100 unit nearly at 25°C. We have since followed this observation more systematically.

(1) The change of refractive index on acetylation is dependent on the hydroxyl group, and it was interesting to find that concentrates containing various quantities of ricinoleo-glycerides showed differences which closely paralleled their acetyl values:

	<i>Acetyl value</i>	<i>Change of R. I. at 25°C on acetylation</i>
Castor oil	151.5	—0.0094
Concentrate A	160.2	—0.0099
Concentrate B	142.6	—0.0075

(2) Hydroxy acids showed similar behaviour; we had occasion recently to test the identity of two groups of acids containing mainly hydroxy and mainly oleic-linoleic acids. The R. I. of each group was determined before and after acetylation.

	<i>R. I. before acetylation</i>	<i>R. I. after acetylation</i>	<i>Difference</i>
Group A	1.4682	1.4686	Very small
Group B	1.4727	1.4674	Large

It was clear that group A was substantially free from hydroxy acids which had all gone into group B.

(3) Could the method be used to detect the presence of castor oil in other oils? We prepared artificial mixtures of castor and groundnut oils and found that above 15 per cent of castor, the change of R. I. was sufficiently large to predict the impurity; the curve connecting the drop in R. I. with the percentage of castor oil in the mixture was as shown in Fig. 1. This would help to eliminate the

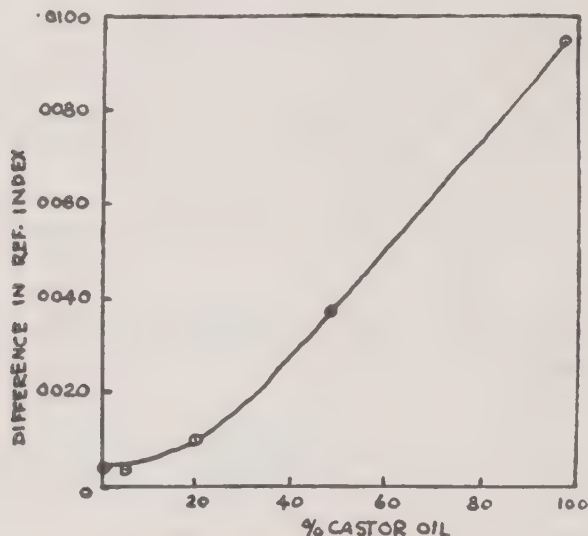


Fig. 1 - Percentage of castor oil in admixture with groundnut oil plotted against difference in refractive indices at 25°C. between the original and acetylated product.

Fig. 1.

tedious determinations of acetyl values by filtration, distillation or saponification procedures.

(4) One possible drawback to the use of the method in practice was the fact that hydroxy acids are known to be produced during the development of rancidity, which might interfere with the method. However a very rancid linseed oil (acid value 23.5) and groundnut oil (acid value 4.1) showed changes of only + 0.0004 and - 0.0001 unit in the R. I. on acetylation, so that rancidity of the oil is not likely to be a disturbing factor.

Concentrating triricinolein from castor oil:

When castor oil is shaken with certain petrol ethers, some of the solvent separates and takes with it a small portion of the glycerides, generally of somewhat greater unsaturation. Since castor oil consists of roughly 75 per cent triricinolein, 15 per cent diricinoleolinolein and 5 per cent each of diricinoleo-saturated and diricinoleodihydroxystearic glycerides, this high I.V. would indicate that linoleic-

rich glycerides are being removed, which is again supported by the lower R. I. of this portion. In a typical extraction we obtained these figures :

	<i>Left</i>	<i>1st Extraction</i>	<i>2nd Extraction</i>	<i>3rd Extraction</i>
Per cent. ...	72	10	10	8
I. V. ...	82.7	89.3	87.0	85.5
R. I. (25°) ...	1.4772	1.4756	1.4760	1.4758
Acetyl value ...	161.2	← 139 - 142 →		

Samples of ricinoleic acid prepared from these triricinolein concentrates analysed very close to theory ; e. g.

	<i>Product</i>	<i>Theory</i>
S. E. ...	297.0	298
I. V. ...	85.6	85.2
Acetyl value ...	166.5	165.0

The method has preparative possibilities in laboratories, and the triricinolein concentrates may find use in lubrication or dehydration. The 3 per cent or so residues are sufficiently similar to castor oil to be used inter-changeably with the latter for most purposes.

Sodium ricinoleate from castor oil :

Sodium ricinoleate is apparently widely used in toothpaste formulations owing to good taste, stability, germicidal properties and the marked lowering of surface tension it produces. Normal soap-making procedures, followed by somewhat excessive amounts of salt for salting out, yielded from castor oil a hard, white soap, which could easily be made in India by any soapmaker having the usual equipment. The costs of the product are made up to a large extent, as is usual, by the price of the oil used, and it should be possible to produce the material at a fraction of the price of the imported material.

Similarly very pure sodium ricinoleate can be made by saponification of the triricinolein concentrates described earlier, to yield a very much purer product than the imported material at a far less price, as the isolation of triricinolein requires only simple equipment and the extra cost is only that involved in recovery of solvent.

The estimation of component fatty acids in oils containing hydroxy fatty acids :

The literature indicates that the analyses of oils containing hydroxy fatty acids, e. g. grapeseed oil, quince seed oil., etc, has always been unsatisfactory. A recent method for analysis of castor oil by Gupta, Hilditch and Riley¹ is based on acetyl values, ethyl acetate precipitation and spectrophotometric study; the latter especially, is a technique not easily accessible in India, and moreover castor oil is exceptional in having the hydroxy acid in over 90 per cent concentration. A routine analytical method seemed desirable, and in this we have succeeded; using a synthetic mixture of groundnut oil fatty acids (70 per cent) and pure ricinoleic acid (30 per cent); three main steps are involved :— (a) Separation of saturated acids by the usual lead salt alcohol method, and subsequent methylation and fractionation.

(b) Separation of ricinoleic from normal unsaturated acids (oleic and linoleic) was necessary as otherwise during ester fractionation a mixture of three components not amenable to mathematical calculation would distil over. The lead salts of the hydroxy acids are known to be insoluble in petrol ether and the literature states that they may be separated from other acids by this means; we found however, that in practice mixed salts of the divalent lead were formed, the separations that occurred being incomplete and completely useless from our point of view. Various differential solubility methods using petrol ether also proved fruitless. Using the new reagent urea, which gave insoluble adduct with oleic and partly linoleic acid but not with ricinoleic, separation of these two groups was, however, simply effected. Methylation and fractionation of the acids from the precipitated urea adduct indicated that the former consisted of about 90 per cent oleic, 6 per cent linoleic and 3 per cent residual saturated acids.

(c) The urea adduct soluble group consists of ricinoleic and linoleic acids, the methyl esters of which boil at similar temperatures under reduced pressures. Acetylation of these methyl esters, while leaving the linoleate unaffected, raised the boiling point of the ricinoleate by about 35°C (at 10 mm. pressure), lowering in consequence the I. V. to 71.7 and the apparent S. E. to 177.0. Fractionation of these acetylated methyl esters gave fractions progressively richer in ricinoleate, with a sharply falling sequence of iodine values and saponification equivalents, and were easily calculated on an I. V. basis; the final figures indicated 70 per cent ricinoleic and 30 per cent linoleic acid in the original mixture.

The figures from the three fractionations on assembly showed excellent agreement with the calculated composition, e. g. ricinoleic acid, experimental 29.9 per cent, theory 30.0 per cent. It will be noticed that at no stage in the above analysis are acetyl values necessary, and the method brings the hydroxyacid oils into line with other fats from the analytical point of view.

References :

- 1, Gupta, S. S. and Hilditch. T. P. ; J. Sci. Food Agri. ; 1951, 2. 445.

DISCUSSION

Dr. S. S. Gupta (N. C. L.) congratulated Dr. Achaya on the new method he had developed for the determination of hydroxy oils especially castor oil. He pointed out that the usual ester fractionation method, due to the dehydration and subsequent polymerisation of the methyl esters, could not be used for the analysis of oils having hydroxy acids. He was experiencing that difficulty in his work on castor oil and other allied oils as from *Sterculia foetida*, the seed oil of which contained about 40 per cent of hydroxy acids. He wanted to know Dr. Achaya's experience about the distillation of acetylated methyl esters of hydroxy acids.

Dr. Achaya replied that the distillation of the methyl esters of ricinoleic acid could be done by him without any difficulty and there was no dehydration or polymerisation taking place whatsoever. Regarding the difficulty of three components distilling over that had been overcome by their new method using urea. By the use of this reagent they were able to separate oleic acid on the one hand and ricinoleic and linoleic acids on the other. After that, by simple fractional distillation the various acids were calculated by the determination of their iodine values.

DEHYDRATION OF CASTOR OIL BY SUBSTITUTED SULPHONIC ACIDS & THEIR SALTS AS CATALYSTS

BY

DR. K. K. DOLE

Fergusson College, Poona.

Dehydration of castor oil is catalysed by a large variety of catalysts, which are classified as follows: sulphuric acid and its salts, phosphoric acid and its salts, oxides and oxy-acids of metals, metallic soaps, some of the fatty acids, dimethyl and diethyl sulphates, sulphonic acids and their salts, some of the organic acids and acid clays.

This classification is not very precise and sharp, but it will serve as a guide for the types of the active catalysts which have been used so far.

In the present investigation, work has been concentrated on sulphonic acids and their salts as catalysts. Sulphuric acid can be considered as hydroxy sulphonic acid thus, $\text{OH}-\text{SO}_2\text{OH}$; or sodium bisulphate, which is one of the well known catalysts for dehydration can be considered as $\text{NaO}-\text{SO}_2\text{OH}$. While benzene sulphonic acid can be represented as: $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$ or the general formula of a substituted sulphonic acid can be written as $\text{X}.\text{SO}_2\text{OH}$. Following sulphonic acids have been investigated so far and investigation on many others is proceeding in the laboratories of the Fergusson College, Poona: benzene sulphonic acid, *p*-toluene sulphonic acid, *p*-xylene sulphonic acid, *o*-phenol sulphonic acid, sulpho-salicylic acid, sulphanilic acid, *m*-sulphobenzoic acid, mixed alkane sulphonic acid, methane sulphonic acid, ethane sulphonic acid.

The free acids were found to be active catalysts. They produced rather dark coloured dehydrated castor oil with high percentage of conjugation. The acid number of the resultant oil produced by free sulphonic acid was also high indicating that the fatty glyceride was decomposed to a certain extent.

A large number of salts of the above sulphonic acids and some others were also investigated. All except one, i.e. potassium *o*-phenol sulphonate, were inactive. This salt, however, was found to be active

enough to give complete dehydration of the castor oil without much decomposition. Besides the product obtained was of a pale colour.

Experimental :

The dehydration was carried out both under atmospheric pressure and reduced pressure. The temperature of the dehydration was varied between 200°C to 300°C according to the nature of the catalyst.

The extent of dehydration was followed by determining the iodine values from time to time by the Woburn's methods since it is well known that Wijs method yields low values in the fatty glycerides, containing conjugated double bonds.

In addition to iodine value, following characteristics were also determined of all the products : hydroxyl value, molecular weight, percentage conjugation, refractive index, viscosity and drying time of the oil with a suitable drier.

The percentage of conjugation of some of the samples of the dehydrated oil was determined by studying the absorption spectra of the oil in ultraviolet region.

Results :

TABLE I.

Dehydration at atmospheric pressure

Catalyst acid	Temp. °C	Percentage catalyst	Time, Mins.	iodine value	Hydroxyl value	acid value	conjugation %
Benzene-sulphonic ...	225	0.3	60	147.3	51.0	37	25.0
<i>p</i> -toluene sulphonic ...	250	0.3	60	138.0	60.9	16.6	18.0
<i>p</i> -xylene sulphonic ...	250	0.3	60	123.7	93.1	6.0	—
Sulphanilic ...	290	1.0	60	130.0	43.0	17.0	—
Salicyl Sulphonic ...	250	0.3	60	138.8	39.0	15.7	18.8
<i>m</i> -sulpho benzoic ...	250	0.3	40	151.2	30.3	40.0	28.8
<i>o</i> -phenol sulphonic ...	250	0.3	60	148.1	55.0	7.4	15.0

TABLE II.
Dehydration at Reduced Pressure

Catalyst acid	Conditions			Pressure mm.	I. V.	H.V.	A.V.
	Temp. °C	Catalyst %	Time-Min				
Benzene sulponic ...	250		70	25	130.0	61.3	8.3
<i>p</i> -toluene sulponic ...	250	0.3	70	25	140.0	38.1	6.8
<i>p</i> -xylene sulponic ...	250	0.3	60	20	124.0	81.1	3.8
Salicyl sulponic ...	250	0.4	60	20	144.2	—	—
<i>m</i> -sulphobenzoic ...	250	0.3	100	25	137.0	58.0	12.1
<i>o</i> -phenol sulponic ...	250	0.3	60	20	148.1	50.0	7.4

Rate of dehydration of the oil is given in the next table III, the velocity being assessed by the estimation of iodine value by Woburn method.

TABLE III

Catalyst acid	Time in minutes						
	10	20	30	40	50	60	70
Benzene sulphonic ...	107	119	128.4	135	142	146	146
<i>p</i> -toluene sulphonic ...	106.5	108.3	118	129	132	136	138.4
<i>p</i> -xylene sulphonic ...	100	—	107	—	—	—	123.7
Salicyl sulphonic ...	109.8	117	123	130	132	134	138.8
<i>m</i> -sulpho benzoic ...	110	130	—	150	152	152.3	...

Sodium salts of a large number of sulphonic acids were employed as catalysts but all except one were found to be inefficient. The temperature of the trial experiments ranged between 250-300°C and the concentration of the catalysts ranged 1-2 per cent. In no case the iodine value beyond 107 was obtained with the exception of one salt which showed higher activity. Sodium salts of the following sulphonic acids were used as catalysts: benzene sulphonic acid, *p*-toluene sulphonic acid, *p*-xylene sulphonic acid, naphthalene sulphonic acid, *o*-phenol sulphonic acid, *m*-nitrobenzene sulphonic acid, 2-naphthol 1-sulphonic acid, 2-naphthol 6-sulphonic acid,

2-naphthylamine sulphonic acid, 1-naphthylamine 2-sulphonic acid, 1-naphthol 5-sulphonic acid, anthraquinone 2-sulphonic acid, anthraquinone 2-6 di-sulphonic acid, anthraquinone 2-7 di-sulphonic acid, *m*-sulpho benzoic acid, sulpho salicylic acid.

Above salts remained solid without melting during the process of heating. The sodium salt of *o*-phenol sulphonic acid did show some reaction above 300°C but the reaction was accompanied by large decomposition due to the high temperature. On the contrary potassium salt of *o*-phenol sulphonic acid is active at 270°C. It gives complete dehydration in about 60 to 70 minutes. The results of this catalyst are summarized in the Tables IV and V.

TABLE IV

Percentage catalyst	Temp °C	Time in minutes					
		20	40	60	80	90	100
1.0 ...	265	109	124	133	135	136	138
2.0 ...	270	120	138	144	146	147	—
3.0 ...	270	130	145	151	153	152.3	—

Above table shows the rate of dehydration at atmospheric pressures. The table indicates iodine values by Woburn method. The behaviour of the catalyst at 20 mm pressure is summarized in the next table V.

TABLE V

Catalyst %	Temp. °C	Time (min.)	Iodine value	hydroxyl value
2.0 ...	290	90	139.5	47
3.0 ...	280	70	127	76
3.0 ...	260	90	125	78
3.0 ...	275	90	134	55
3.0 ...	280	90	147	43
3.0 ...	285	85	154	15

It should be noted that at reduced pressure, temperature and period required for the same amount of dehydration are increased than at ordinary pressure. Similarly, if the period of heating with the catalyst is prolonged some polymerisation takes place.

Instantaneous Dehydration :

Above results indicate that sulphonic acids can act as good catalyst for the dehydration of castor oil. Since salts of these acids are not useful as catalysts it seems that the mechanism of catalyst is the one suggested by Forbes and Neville¹. The acidic groups of the catalyst formed an intermediate ester with the hydroxy group of the ricinoleic acid with the removal of water. The intermediate ester subsequently breaks up at high temperature with regeneration of the catalyst and production of a double bond in the fatty acid part of the oil. Assuming this mechanism to be correct we selected acidic substances containing more number of acidic groups which are capable of forming intermediate esters and tried under varying conditions. Most of the catalysts used so far in the dehydration of castor oil are insoluble in the oil and the reaction mostly takes place in heterogeneous phase. A very intimate contact of the catalyst is essential if it is to be useful for the dehydration. This was achieved by developing catalyst which were soluble in volatile solvents which in their turn were soluble in castor oil. On mixing the solution of the catalyst in the oil good dispersion of the catalyst was obtained which gave increased facility for the reaction. Then selecting some what higher temperatures it was possible to hasten the reaction of dehydration to considerable extent. At present it is possible to dehydrate the castor oil in a short period of two minutes and the iodine values of such oils have been found to be of the order of 150-155. Percentage conjugation is found to be of the order of 20-28 and drying properties of such oils are similar to those produced by ordinary catalyst. So large number of active groups in the catalyst, thorough its dispersion in the oil and high temperature helped to dehydrate the castor oil.

References.

1. Forbes & Neville ; *Ind. Eng. Chem.*, 1940, 32, 3959.

DISCUSSION.

Mr. N. S. Bharatia asked Dr. Dole whether he had tried α -naphthol sulphonic acid as a dehydrating catalyst because this compound gave very pale coloured dehydrated castor oil. Moreover if dehydration of the oil be carried out in presence of sulphuric acid in the atmosphere of carbon di-oxide, reasonably pale coloured oil was obtained. He further suggested that iodine value would not be the criterion for the extent of dehydration as conjugated double bond acid obtained during dehydration of the oil would not give the correct value.

Dr. Dole replied that besides the iodine value they could find out the extent of dehydration by the amount of water liberated or the determination of the hydroxyl value. He also exhibited a sample of dehydrated castor oil that he prepared, in order to show its colour.

DEHYDRATION OF CASTOR OIL

BY

M. A. SIVSAMBAN, DR. S. A. SALETORÉ & DR. S. H. ZAHEER

*Central Laboratories for Scientific & Industrial Research,
Hyderabad (Deccan).*

Dehydration of castor oil, by which an absolutely nondrying oil is converted into an oil of highly desirable drying properties, which Terrill' calls "a dramatic fact in itself" is now a well established industry in the Western countries. The rapid growth of this industry may be seen from the fact that while America consumed 15.6 million pounds of the same in 1943, in the year 1949 this figure had increased to 31.4 million pounds representing approximately 33.3 per cent of the total consumption of the castor oil in the U. S. A. Since then the consumption must have gone up further, if Indian exports of the seed and oil are any guide.

India, however, does not seem to have taken up either the manufacture or utilization of dehydrated castor oil. With an annual production of about 126,400 tons of castor seed out of a world production of about 321,800 tons², India is today a major producer of the oil seed. There is no evidence to show that any of the oil is used in the paint and varnish industry. Since dehydration of oil in India itself, can give rise to a stable small sized industry, this investigation was undertaken.

A review of scientific literature shows that there is no dearth of recommended catalysts for the dehydration, the number of same published, literally running into hundreds. But a closer examination reveals that most of the work done concerns itself only with the extent of dehydration obtained, and does not go into the very many other aspects which are essential for a practical undertaking. Further, published literature does not give the practical details so very necessary for actual operation on an industrial scale. If we look at the problem from the point of view of establishing an industry in India, the availability and cost of catalyst assume primary importance. Then again, there is the question of the colour of the product. Catalysts which are cheap and available may affect the colour of the product adversely and while the colour may not be much in experiments carried out on the laboratory scale, it has a tendency to become more

when carried out on an industrial scale due to a variety of reasons. Since D. C. O. is best used for manufacture of white enamels, it is obvious that if the product is coloured, however good the dehydration may be the product will not sell. Next is the question of after tack, when the film dries. It is an acknowledged fact, that one of the serious drawbacks of D. C. O. is its after tack, and according to Wilson³ the best method so far has been to mask this defect by means of co-polymerization, and no satisfactory method of reducing tackiness itself has been reported. The investigation carried out by the authors, therefore, does not open up any new theoretical line of work but mainly covers known grounds, with a view to tackle difficulties of practical importance.

Hyderabad state has good deposits of clays similar to Fuller's earth at a place called *Vicarabad*. The laterite clays are a peculiar type of residual clay formed by the weathering of different rocks, in which aluminium hydroxide and iron hydroxide predominate and silica has been largely eliminated. Dehydration experiments with these clays have given good results, the product being very pale in colour and having excellent drying properties. They, however, suffer from a drawback in that 12 to 15 per cent of the clays have to be used, resulting in heavy loss of oil due to retention by the catalyst. Activation of the earths was next tried and it was found that while activation reduced the time required for dehydration, there was no material improvement in the quantity of catalyst required.

Attention was, thereafter, given to the use of sodium bisulphate which according to reports is the catalyst commonly used in America. Laboratory tests showed that sodium bisulphate gave good dehydration when used in quantities of 1.5 to 2 per cent on the weight of oil, but the D.C. O. produced was comparatively dark in colour, and had some after tack, besides having a high acid value.

During the experiments careful observations revealed an interesting feature. If a batch of oil say of 1000 grams was dehydrated, and it took $1\frac{1}{2}$ hours from start to finish inclusive of heating time to complete the dehydration, there was very little noticeable change in colour during the 45 minutes period of initial heating, that is the time taken from start till the temperature of dehydration was reached. The same could be said of the period during which dehydration actually took place, while a rapid darkening was visible immediately the reaction was over.

Although it is not possible to use the catalyst over and over again due to the impossibility of isolating the acid formed from the product of the reaction, there is evidence to show that the catalyst is

regenerated and can be used over again. Thus, if fresh raw oil were added drop by drop to the initial batch, immediately dehydration of the same is over, it is possible to dehydrate more oil without any addition of fresh catalyst. For example, in one experiment, while 2 per cent sodium bisulphate dehydrated 200 grams oil, and anything less than 1.5 per cent was not enough to give complete dehydration, by adding fresh oil to the batch immediately it was dehydrated, it was found possible to dehydrate with a catalyst strength of as low as 0.6 per cent on the total oil used with the further advantage of a much lighter colour.

As regards tackiness it has been noticed that the presence of non-glyceridic matter and free fatty acids determines to a great extent whether the final D.C.O. is tacky or not. Unfortunately there are no established methods for evaluation of tackiness. But examination by the finger method of samples produced by us and imported samples shows a big difference in so far as tackiness is concerned. Experiments were then carried out on a locally rigged out pilot plant on 30 lbs. of oil charge and similar results were obtained.

Results of the drying tests for our laboratory and pilot plant samples and the imported sample are as follows :—

The samples were all brought to the same viscosity for the drying tests (46 poises at 25°C) 0.05 per cent cobalt drier and 0.5 per cent lead drier were added and equal quantities of turpentine.

While our Laboratory and pilot plant samples dried in an equal time to the imported sample i.e. 2 hours, they became non-tacky within one hour after this where as the imported sample remained tacky for days afterwards.

Other analytical results for the above samples were as follows:—

	I. V. (Hanus)	I. V. (Woburn)	Acid Value	Viscosity 25°C
Laboratory samples : ...	133.8	149.2	2.97	3 poises
Pilot Plant sample : ...	130.3	139.7	5.22	12.9 „
Imported sample (1) : ...	113.7	129.7	23.7	3.5 „
„ „ (2) : ...	113.2	130.5	15.3	5.5 „
„ „ (3) : ...	102.4	129.6	23.8	45 „
„ „ (4) : ...	107.7	122.4	23.3	46 „

It will be noticed that our samples are much lower in acid value and have a higher Woburn iodine value than the imported samples.

Further work on the subject is in progress.

REFERENCES

1. Terril, R. I., *J. Am. Oil. Chem. Soc.*, 1950, 27, 677.
2. Indian Central Oilseeds Committee *Report of Progress in oil Technology*, December, 1950.
3. Wilson, R. J., *Oil & Colour Chemists Association*, 1950, 33, 503.

PROSPECTS OF SYNTHETIC OILS IN PAINTS AND VARNISHES

BY

R. K. BANERJI

Murarka Paints and Varnish Works Ltd., Calcutta.

As is well known, commercial paints and varnishes can be classified into two broad groups: One, depending on the property of certain vegetable oils with or without the aid of certain chemicals as driers to form dry films having certain desirable properties when exposed in thin layers to air; and the other depending upon the formation of a layer of solid materials of the resin type left after the evaporation of the solvent in which the materials had been dissolved. These are called lacquers.

Oils can be broadly divided under three heads:—

- (1) Oils of vegetable origin,
- (2) Oils of mineral origin,
- (3) Synthetic oils.

The mineral oils, as a class are non-drying. Uptill now, our work on an industrial scale was concerned mainly with vegetable drying oils e.g. Linseed, Tung etc., but we cannot afford to waste the semi-drying oils and non-drying oils of vegetable and mineral origin.

With a view to utilize these products, we became interested in finding out the possibility of converting the usually available mineral oils into liquids which when exposed in thin layers in the air would behave in the same way as linseed or other drying oils.

During the course of our experiments, we found that when these non-drying mineral oils or semi-drying vegetable oils are subjected to a peculiar process of chemical treatment at a suitable temperature in presence of a suitable catalyst and then removal of excess of reagents, liquids are obtained which when used as a medium for making paints have given quite satisfactory films as those of paints based on linseed oil.

We have tried this medium in the preparation of paints in exactly the same way as is done with linseed oil and we find that mineral oil based paints are quite as satisfactory as the others. The detailed practical tests of the film under exposure to open atmosphere

are going on and after a lapse of four months the painted surfaces have shown no sign of deterioration.

It might be of great interest to us at this stage to know whether there is at all any possibility of the paint industry standing in need of finding a substitute for the common drying oils like the linseed, tung etc. An expression of opinion in this matter from the Director, National Chemical Laboratory, would be of considerable benefit to workers in this line.

At present Government specification for paints and varnishes especially mentions the use of no other oil but linseed or in special cases tung oil or dehydrated castor oil, and unless some latitude is given in the specifications for the use of certain quantities of other medium, it would not be possible for any investigation on an economic basis to be carried out in any industrial concern.

It needs hardly be said that if the use of oils other than vegetable oils to certain extent becomes permissible in the composition of paints these materials would become less costly and be a great saving to our country.

DISCUSSION

Mr. N. S. Bharatia of the Elephant Oil Mills wanted to know from Dr. Banerji about his source of mineral oil and how these synthetic oils would be cheaper than linseed oil.

Dr. J. S. Aggarwal also pointed out that the only mineral oil source in India was Digboi in Assam where the production was not more than 8 per cent of the total consumption of these oils in this country. Moreover, how a mineral oil could be changed into a paint drying oil.

Mr. Banerji informed that the spindle oils, which were employed, were obtained from M/s Burmah Shell from Digboi. The synthetic oils prepared from them dried very nicely and as the spindle oil was cheaper than linseed oil, the synthetic drying oils were very cheap.

DRIER EFFECTS ON DRYING OF OIL FILMS

BY

DR. S. A. SALETORÉ, A. HAI AND V. R. HARWALKAR

*Central Laboratories for Scientific and Industrial Research,
Hyderabad (Deccan).*

According to Klebsattel¹ "The Chemistry of drier action is a subject concerning which surprisingly little is known". Then again he states, "probably no phase of paint and varnish technology is so empirical and so devoid of a scientific background as the subject of paint driers in general. Fundamentally paint driers have not changed for centuries (Mattiello Vol. 1 pp. 533). The only improvement made in driers during the last 50 years has been the production of more uniform and more soluble driers, by combining the same old metals with new organic bases like linseed oil fatty acids and naphthenic acids.

Driers generally used in practice are the soluble salts of Pb, Mn, Co, such as rosinate, linoleate, and naphthenate. Their use in small quantities (0.01 to 0.5 per cent as metal) greatly accelerates the so called drying of oil films. Driers are known to cut down the induction period and increase the rate of oxidation giving a dried film with a lesser intake of oxygen. They are also believed to influence the polymerisation of the oil to different degrees. Thus lead is stated to be more of a polymerisation catalyst than an oxidation catalyst, while cobalt is quite the reverse and manganese occupies an intermediate position with properties of both to some extent.

A great deal of work has been published in previous years on the influence of driers on drying of oils. Thus for example Micholson and co-workers have examined various factors which affect the rate of drying such as Iodine value of the oil, amount and type of driers, acidity of the oil, nature of incident visible light and composition of the atmosphere. But most of this earlier work has been based on a single idea, namely, that the drying of oils is mainly an oxidative reaction which we now know is not quite true. It is, therefore, not very surprising that very few attempts have been made to study the catalysis of other processes involved in "drying" and whatever little work has been done has proceeded on the hypothesis that the only other reaction is polymerisation.

More recent work on unsaturated fatty esters and glycerides has thrown a good deal of light on the mechanism of oxidation and shown how peroxides or hydroperoxides are first formed and how these could break up and how isomerisation to form conjugated structures also take place. Various theories have been put forward to explain subsequent changes swinging from C-O-C linkages to C-C linkages giving rise to linear growth, cross linked polymers and cyclic esters as a result of intermolecular and intramolecular reactions. But most of this work has been carried out on oils in the absence of driers. Hence what happens when driers are present; to a great extent is still an unexplored field. Work specifically referring to the action of driers is limited to only a few publications. Mention may be made of one by Skellon and Spence² on the influence of the acid radical of driers on film formation, another by Jackson and Kummerow³ on the action of metallic naphthenates on the formation and destruction of diene conjugation in fatty acids and a third by Bowles⁴ on the effect of pure naphthenates on evaporation, flocculation and gelation of stand oil varnishes.

The present investigation was taken up in the Central Laboratories, Hyderabad, with the idea of re-examining the behaviour of known driers through the various stages of drying of linseed oil and studying the catalysing and synergistic effect of different organic chemicals in order to have a clearer picture of what takes place and if possible of achieving more improved drying. The present paper deals with only a preliminary study of the action of oxygen on linseed oil films; hence the inferences drawn should be considered as tentative.

The technique employed was simple and consisted of observing manometrically the absorption of oxygen by a known quantity, (about 1 g.) of linseed oil contained in a 2 litre flask maintained at a steady temperature of 96°C. Readings were taken with and without a soda lime tube in between the manometer and flask to note the extent of the absorbable volatile matter produced by oxidation, and obtain corrected figures for absorption of oxygen only. The first few experiments were carried out on the oil samples spread out at the bottom of the flask with and without known quantities of cobalt and lead driers dissolved in the same. As the thickness of the film and area of exposure per unit weight were found to materially affect the results, an improvement was made in the technique in subsequent experiments by taking up the oil in 20 g. of dry quartz sand of 40-60 mesh. Driers used were lead and cobalt as oleates, freshly prepared each time. In every case readings were taken at intervals of time, till there was no further noticeable absorption (about 5 hours). Graphs were then drawn relating oxygen absorption with time.

After the experiment the sand in each case was extracted with low boiling petrol ether, and then with acetone and the extract examined.

Discussion of Results :

- (1) Results obtained with and without sand vary a great deal not only in the extent of absorption of oxygen which may be expected but also in the type of curve. Hence the nature of the final dried film does appear to be influenced by its thickness. Incidentally, this shows up how the technique employed for study of drying phenomena requires careful consideration, and how results obtained by previous workers employing technique involving large quantities of oil as for example bubbling oxygen through a mass of oil are likely to be misleading.
- (2) The data obtained with and without the soda lime tube are interesting in that they show the extent of breakdown which takes place. In one particular instance as against oxygen absorption equivalent to 20 mm, the pressure due to absorbable gases was 17 mm. indicating that the breakdown of the oil molecule was by no means negligible, as persistently maintained by majority of earlier workers. From this it follows that reaction between the residual products of oxidation are also likely to be important when considering the mechanism of film formation. The data given by Long, Rhineck and Ball⁵ as long back as 1933 indicating a production of 28 per cent of volatiles at 52°C. supports our contention and deserves better appreciation. Of course it goes without saying that drying at lower temperatures would be less drastic in action.
- (3) The curves obtained with lead and cobalt driers in addition to confirming the known fact that driers cut down the induction period during which there is little or no absorption indicate the existence of 3 other phases, the first of rapid absorption, the second of absorption at a reduced rate and a final phase of quiescence when absorption is negligible and not detectable by the methods employed. They also show that oxygen absorption is less in the presence of driers and varies with the drier used. Another observation of interest is that while the period of the first phase is reduced and the quantity of oxygen absorbed is less during this time when driers are used there does not seem to be any great change in the second phase. During

this second phase, the oil absorbs much less oxygen at rate which progressively becomes slower and slower. From this it would be seen that while driers no doubt hasten the start of the reaction, once oxygen absorption has started, they do not take much part in accelerating the reaction.

Hence if the driers do take any part during these phases, one has to look to reactions other than mere absorption of oxygen.

- (4) Table I gives the analysis of the final product obtained in each experiment after contact with oxygen for 5 hours at 96°C.

TABLE I.

Sample	Type of final product.	Petrol other extract per cent	Acetone extract per cent	Acetone insoluble by difference per cent
Linseed oil only.	Soft, plastic	15	60, sticky, viscous liquid	24.8
Oil-0.1% Co.	Hard, dried	12.9	17.2, non-sticky solid	69.9
Oil-0.5% Pb	Soft, plastic	24.7	67.7, Solid Gel. non sticky	7.6
Oil-0.1% Co + 0.4% Benzoyl peroxide	-----	7.5	24.7	67.8

In the presence of cobalt the acetone soluble is 17.2 per cent as against 60.2 per cent when cobalt is absent, and the acetone insoluble is much more (69.9 per cent) as against 24 per cent. Since cross linked polymers are known to be acetone insoluble, and linear growths are likely to be more soluble, the present data taken in conjunction with what has been mentioned earlier lends strong support to the idea that driers catalyse reactions other than oxygen absorption, and that different driers behave differently.

Conclusions:

While it would be premature to draw any conclusion on the basis of these preliminary studies, the following possible explanations of drying phenomena in the presence of driers appear to be worth considering :

- (1) Driers cut short the induction period, but do not otherwise greatly influence the absorption of oxygen.
- (2) The residual breakdown products of oxidation are not negligible and their reactions have to be considered in film formation.
- (3) Driers play a significant part in reaction following absorption of oxygen.
- (4) Some driers appear to accentuate the production of soft films which are formed at 96°C in the absence of driers, indicating most likely the formation of linear growths; others catalyse the formation of hard films possibly due to cross linked structures.
- (5) If quicker and better drying is to be achieved we have to look to accelerators other than the known metallic driers, which will catalyse reactions other than oxygen absorption.

References:

1. Klebsattel; C. A.; *J. Am. Oil Chemists Soc* ; 1950, XXVII, 500.
 2. Skellon & Spence ; *J. Soc. Chem. Ind.*, 1948, 67, 365.
 3. Jackson, A. H. and Kummerow; F. A ; *J. Am. Oil Chemists Soc.* 1949, 26, 460.
 4. Bowles, J. ; *Oil and Colour Chemists Assoc.* 1950, 23, 356.
 5. Long, J. S., Rheineck, A. E. and Ball G. L.; *Ind. Eng. Chem.* 1923. 25, 1086.
-

TOBACCO SEED OIL AS A POTENTIAL RAW MATERIAL IN SURFACE COATINGS

BY

P. GOPAL SHARMA

National Chemical Laboratory, Poona

India holds an important position amongst the tobacco-producing countries of the world. The major tobacco producing zones in the country are Bihar, Bengal and Madras. In the Guntur and Krishna districts of Madras State 1,50,000 acres are under tobacco cultivation which yield 10,000 tons of seed. Though the oil content of the seed is generally between 35 and 37 per cent, yields obtained by expression generally vary from 28 to 30 per cent. Thus, if the entire seed is collected and crushed, about 2,500 tons of oil would be obtainable in Madras state alone.

On recent enquiries, the Government of Madras reported that the potential supply is estimated at 8,100 tons of tobacco seed per annum. The importance of the seed was recognised only during war years and collection on a commercial scale was made only from 1949 onwards. The production of oil was about 1,000 tons, or half of the quantity available from existing resources. Almost the entire quantity produced was exported.

Tobacco-seed is not known to be collected for the extraction of oil in Bihar.

Tobacco-seed oil has an iodine value 132 to 146 and contains about 75 per cent of linoleic acid and no linolenic acid. The linoleic acid rich samples of the oil should serve as good drying oils; and such oils have one great advantage over linolenic acid rich oils in that the coating films of varnishes and paints prepared from such oils do not turn yellow on long exposure.

The oil is free from nitrogen and any toxic material. If refined properly it may be used for edible purposes, and is similar to safflower and *til* oils. It has been compared to cotton seed oil and, butter in digestibility. Besides edible utility, it is a good illuminant and gives a smokeless flame. Properly hydrogenated oil should serve as a cheap raw material in soap industry.

Rao and Ramanayya¹ prepared double boiled, blown, stand and polymerised tobacco seed oil. Films with better lustre and greater flexibility than those obtained from linseed oil were obtained. They found that the films developed tackiness on standing.

A good deal of work has been carried out at the National Chemical Laboratory, Poona on the utilisation of the tobacco seed oil for various coating compositions.

Sharma, Budhiraja and Aggarwal² have been engaged for some time past trying to remove the defects mentioned by Rao and Ramanayya. They preferred to use isomerized oil as it is known that when linseed oil is isomerised, its drying qualities are much enhanced. For this purpose the oil is heated with quinones, activated nickel-carbon and activated silica. The films of these treated oils dry in 3 to 4 hours with almost no tackiness. The isomerized oils are pale yellow or pale brown and the films are more lustrous, flexible and resistant to water, alkali, mineral acids and organic solvents, than those obtained from linseed oil. A very important feature of such films is that there is a very slight blushing after long contact with water, and this blushing completely disappears on drying the film in air, and it regains its original gloss, flexibility and hardness whereas in the case of linseed oil films, the blushing is heavy and permanent. Titanim dioxide paint films retained whiteness and gloss even after keeping for one year.

Sethi and Aggarwal³ prepared zinc, calcium, magnesium and manganese salts from polymerized fatty acids of isomerized tobacco seed oil by usual methods. Varnishes prepared from these resins gave quite hard and glossy films. They were sufficiently resistant to water, alkali, mineral acids and organic solvents. Water-proof cloth prepared from these varnishes did not allow water to pass through, even after 100 hours.

Sarin and Kapur⁴ have succeeded in replacing linseed oil fatty acids completely with tobacco-seed oil fatty acids in the preparation of alkyd resins and baking wrinkle finish coatings.

Besides synthetic resins and baking wrinkle finishes, considerable work has been done by Sharma and Aggarwal on the use of tobacco seed oil in the production of air drying wrinkle finishes⁵. These coatings require highly drying oils such as Kamala seed oil, Tung oil etc. Isomerized tobacco-seed oil could safely be used upto 75-80 per cent in admixture with Kamala seed or Tung oils in the preparation of air drying wrinkle finishes. Wrinkle patterns of regular and beautiful designs and good flexibility can be obtained with admixture with tobacco seed oil as from Kamala seed or Tung oils alone. These varnishes can be used for the production of frosted glass, rexine and for other decorative coatings.

Work on the utilisation of tobacco-seed oil as such, instead of its fatty acids, in the preparation of synthetic resins is in progress in this Laboratory.

Apart from surface coating materials, tobacco seed oil is found to be a potential raw-material for the manufacture of factice. Such materials have been successfully prepared by Rao in this Laboratory.

It would not be out of place if mention is made of the seed cake. The tobacco seed cake constitutes 60 to 70 per cent of the seed. It contains 26-36 per cent protein, 32 per cent carbohydrate, 5-7 per cent oil and 20 per cent crude fibre. It is also rich in potash and phosphorus, (P_2O_5 7.15 per cent, K_2O 5.47 per cent on the weight of the ash). It can serve as an important raw material in the plastic industry.

In the light of aforesaid technical utilisation to which tobacco-seed oil can be put, it is evident that the seed and the oil could be a valuable asset to this country.

References :

1. Rao M. V., and Ramanayya S. V., *J. Sci. and Ind. Res.*; 1948, 7, 87.
2. Sharma P. G., Budhiraja N. C. and Aggarwal J. S., *J. Sci. and Ind. Res.*; 1951, Vol. XB. No. 2, 33-36, *India. Patent* No. 42885.
3. Sethi, S. C. and Aggarwal J. S., *J. Sci. and Ind. Res.*; 1951, Vol. X-B, No. 9, 205-208. *Ind. Pat.* No. 43164.
4. Sarin K. K. and Kapur S. L., *J. Sci. and Ind. Res.*; 1951, Vol. X-B, No. 4, 94-97, and *J. Sci. and Ind. Res.*; 1951, Vol. X-B, No. 7, 168-170.
5. Sharma P. G. and Aggarwal J. S., *Paint India*, Sept. 1951, 10-11, and 34, *Ind. Pat.* 44737, *U. K. Pat.* 208345 (1951).

DISCUSSION

Mr. M. B. Satyanarayanan of the Addison Paints and Chemicals Works, Madras wanted to know the time that the air drying wrinkle finish varnish film took to get dry.

Mr. Sharma replied that the film became touch dry in three to four hours and hard dry in two days. If the drying temperature was kept at 50-60°C, the film dried very rapidly.

UTILISATION OF VEGETABLE OILS FOR THE PREPARATION OF ALKYD RESINS FROM TETRACHLORO PHTHALIC ANHYDRIDE

BY

DR. D. J. MEHTA

National Chemical Laboratory, Poona.

Recently the large scale commercial production of Tetrachloro phthalic anhydride (T. C. P. A.) has made this material of increased interest for the manufacture of oil modified alkyd resins. Not only tetrachloro phthalic anhydride has higher melting point than phthalic anhydride but it has four chlorine groups in the benzene ring to help to manufacture fire retardent paints.

Little work has been published on the use of T. C. P. A. in the conventional oil modified type of alkyd resins; however, it is generally known that alkyds made with T. C. P. A. instead of phthalic anhydride, are darker in color. In general, the intensity of color difference increased as the unsaturation in the oil increases. For example, linseed oil T. C. P. A. alkyd are very much darker in colour than soya bean and coconut oil alkyd modified resins. Maleic anhydride has been used to obtain improved color with P. A. alkyds and similar results are obtained with maleic anhydride in T. C. P. A. alkyd resins. However, the best overall results were obtained with maleic anhydride and oxalic acid, even though oxalic acid alone did not improve the color significantly.

The alkyd resins were made by the usual fatty acid process, in which T. C. P. A., glycerol and fatty acid are placed in the kettle and processed at a temperature from 430 to 450°F until the desired acid number and viscosity have been reached.

Alkyd resins were also made with P. A. and T. C. P. A. as the dibasic acid, glycerol as the polyhydric alcohol, and with linseed, soya bean and coconut oil fatty acids as the oil modifier.

Improvement of colour:

Attempts were made to improve the colour of the resins by adding up to 2 per cent of various materials. These include maleic anhydride, fumaric acid, oxalic acid, ammonium oxalate, zinc oxide, lead monoxide and magnesium oxide. The addition of 2 per cent maleic anhydride produced a marked improvement in colour, particularly with linseed modified alkyd resins, but it introduced a tendency of reactivity. Somewhat better colour was obtained with a

combination of 1.5 per cent maleic anhydride and 0.5 per cent oxalic acid and this combination appeared to be free from any objectionable reactivity.

Resin containing T. C. P. A. and resin containing P. A. were compared for air drying time and film properties of hardness, flexibility, water and alkali resistance. Resin containing T. C. P. A. was slightly poorer than resin containing P. A. except alkali resistance. A test in 1 per cent caustic soda solution showed T. C. P. A. resin to have slightly more resistance than P. A. resin.

Since the principal interest in these resins was their use in fire retardent paints, the formulation for semi gloss house paint was prepared. The fire retardent test was made in accordance with the method developed by the Technical Committee of the New York Paints and Varnish Production Club. The results show some superiority for the T. C. P. A. alkyd paint over the regular P. A. alkyd paint. However, the superiority is not large, due, no doubt, to insufficient chlorine in the dried coating. It is known that higher pigment ratio improves fire retardence, but this would apply equally to P. A. alkyd resin paint. It is not feasible to increase the glycerol T. C. P. A. portion of the resin because it is felt that the experimental resins already contained the minimum oil content for satisfactory application properties. It is known that resinous materials with a chlorine content in excess of 50 per cent are good fire retardent binders, e.g. chlorinated rubber and the highly chlorinated paraffines. Obviously if the oil could be replaced with a highly chlorinated material having comparable air drying and film forming properties, the fire retardent quality of the alkyd would be enhanced considerably.

Soya bean and coconut oils modified alkyds were made by the standard fatty acid process. The experimental soya bean resin was compared with a conventional commercial product (rezyl resin 387-5 American Cyanamid Co.) in connection with 20 per cent and 30 per cent melamine formaldehyde and urea formaldehyde respectively, in white baking finishes; coconut resin was also compared with commercial product (rezyl resin 92-5) in the same amino resin combinations for white baking finishes.

In general, the T. C. P. A. resins baked slightly harder than the commercial standards and they were also slightly superior in alkali resistance but they were inferior in colour and colour retention on heating. Since original colour and colour retention are very important requirements of this type of resin, it was felt that further improvement in colour properties of the T. C. P. A. resins would be necessary before they are satisfactory for this purpose.

CASHEW NUT SHELL LIQUID-A POTENTIAL RAW MATERIAL FOR THE PAINTS AND VARNISH INDUSTRY

BY

H. H. MATHUR

National Chemical Laboratory, Poona

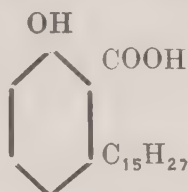
Cashew nut shell liquid is one of the few economic sources of naturally occurring phenols in India. Its industrial importance was first realised in America and is being imported there in large quantities, mainly from India.

The cashew tree grows mostly in tropical areas. In India it grows in abundance along the coastal regions of the Bombay and Madras states upto a height of 2,000 to 3,000 ft. in gravelly areas unsuited for cultivation of other crops. The cashew nut grows from the cashew apple, the nut develops from the flower and subsequently the cashew apple grows between the nut and the stem. The nut has shell about $1/8$ inch thick, inside which is a soft honey comb structure containing a dark reddish brown viscous liquid termed as the cashew nut shell liquid which has a strong vesicant and dermatitic action on the skin. Available statistics show that nearly 60,000 tons of the nuts are annually produced in India. It is estimated that some 15,000 tons of the shell liquid can be recovered annually. As the material could not find adequate use in this country, almost the whole of it has been exported to the United States where it has been established as a starting material of exceptional value for the plastics and paints industry mainly as a result of the researches carried out by Harvey and collaborators¹. Since 1926 a steady stream of patents shows the success with which their work has met.

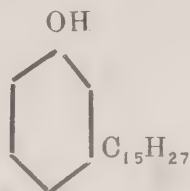
The cashew nut shell liquid was, till recently the exclusive concern of the cottage industries on the western coast of Southern India. The original and native method of isolating the kernel consists of roasting the nuts in an open pan thus charring the cell wall which permits the oil from the ruptured cell to escape. Modern production employs extraction with hot oils which recovers only about 50 per cent of the shell liquid but manual decortication of the nut becomes easy after the processing and the quality of the kernel is not adversely affected by it. After the removal of the kernel a

further quantity of the shell liquid is recovered by the steam distillation of the shells. Siddiqui and Azharali Khan² have patented a process for the expulsion of the shell liquid which consists in exposing the nuts or shells to superheated steam in a closed retort.

The chemical composition of cashew shell liquid was first investigated in 1847 by Stadler³ who isolated two distinct compounds. One of these, an acid which constituted about 90 per cent of the total shell liquid was named anacardic acid, the remaining 10 per cent a phenol was called cardol. Later Ruhemann and Skinner⁴ assigned to the acid the formula $C_{22}H_{32}O_3$ and considered it a hydroxy carboxylic acid. More recently, a detailed study of anacardic acid by Smit⁵ led to its formulation as penta-deca-dienyl salicyclic acid. A fairly exhaustive study by Pillay⁶ suggested for the acid the structure of a salicyclic acid derivative with a penta-decadienyl chain in the ortho position which has been supported by Gokhale, Patel and Shah⁷.



Like other salicyclic acid derivatives, anacardic acid decarboxylates smoothly on thermal treatment and gives a monohydric phenol namely anacardol.



The commercial isolation of the liquid involves a rather drastic treatment resulting in some polymerisation and in the case of monohydric phenol, some loss of unsaturation producing cardanol which differs from the original anacardol in having only one double bond in the side chain. Just where and how this apparent hydrogenation has occurred is not yet known. The remaining 10 per cent of the shell liquid termed as cardol by Stadler³ was studied by Spiegel and coworkers^{8,9} who assigned to it the formula $C_{35}H_{50}O_3H_2O$ and although its constitution was not definitely determined, it appeared from their work to be a phenol.

Harvey and collaborators, have worked out a number of processes for the conversion of the cashew shell liquid into solid or semi-solid resins suitable as starting materials in the varnish and plastics industry. The patented processes are principally based on

the use of concentrated mineral acids, hydrocarbon sulphates, formaldehyde, hexamethylene tetramine and a number of inorganic salts as chemical reactants or catalysts. The plastic material obtained by the various processes are being employed in the U. S. A., alone or in the combination with other resins, in the preparation of insulating varnishes, typewriter rolls, oil and acid proof cold setting cement, industrial floor tile and automobile brake linings and also as a substitute for rubber for certain requirements, alone or in combination with synthetic rubber.

The resin maker first gives a mild chemical treatment with materials such as hydrocarbon sulphates and sulphuric acid which removes metallic impurities and decomposes sulphur compounds present in minute quantities. This treated shell liquid can then be used as the resin making raw material employing various polymerisation methods or can be separated into two portions, the steam distillate containing cardanol amounting to about 70 per cent of the total and the residue containing cardol and polymer formed during the process of extraction and treatment.

The methods employed to thicken or polymerise the shell liquid can in general be classified as follows :—

- I. Polymerisation by physical means: (a) heat, (b) pressure, (c) radiation, (d) electrical discharge.
- II. Polymerisation by Chemical means,: (a) addition of various reagents, (b) oxidation - blowing.
- III. Polymerisation by combination of any two of the above.

Investigations on the industrial utilization of cashew shell liquid were taken up in the laboratories of the Council of Scientific and Industrial Research. As a result of this work a process for the conversion of cashew nut shell liquid in combination with varying proportions of bhilawan nut shell liquid into a semi-solid to solid resin has been worked out and patented by Siddiqui and Azaharalikhani¹⁰. The resins obtained through this process have been utilized for the production of enamels, varnishes, water proofing compositions and moulding powders. Cashew shell liquid has been further employed in the manufacture of cancelling postal stamp and allied inks¹¹. In this connection the remarkable behaviour of resinols (viz. cashew and bhilawan shell liquids) to stabilise the dispersion of the pigments in the vehicle and to reduce the viscosity of the dispersion in the case of a mineral oil medium, whereas an opposite influence on the viscosities of vegetable oils is noteworthy¹².

As a result of the work done at the National Chemical Laboratory, Poona cashew resins have been produced by polymerisation of the shell liquid employing certain reagents to accelerate polymerization along with a heat treatment followed by oxidation by means of blowing air through the mass. The reagents employed were, certain driers, metals, metallic oxides, chlorides and sulphates. The semi-solid plastic resins so obtained are soluble in vegetable oils and common organic solvents and thinners employed in the paints and varnish manufacture. These resins have been utilised for the preparation of baking enamels which have exceptionally high resistance to alkalies, acids and water and are electric insulators. Some of the enamels could stand 5N caustic soda for about 100 hrs. and 10 per cent boiling nitric acid for an hour. Experiments were conducted to find out whether this enamel can substitute tin lining for food containers. Vegetable oils, viz. groundnut, mustard and sesame oils and *Vanaspati* were heated in cashew enamel lined vessels at 100°C for 100 hours with no appreciable increase in acid value or change in colour. The enamel coating was also not affected. The oils thus heated were fed to rats and the average increase in weight of rats fed with this oil during a period of 10 weeks was 30 gms. as against 33 gms. for rats fed on groundnut oil similarly heated in glass vessel and 54 gms. for rats fed on raw groundnut oil. The only noticeable effect on the growth rate was between the heated and the raw groundnut oil which is due to the effect of heat treatment on the nutritive value of the oils.¹³ The average food intake of the animals was comparable in all the three groups. From these experiments it can well be concluded that the Cashew enamel would substitute tin metal, which is not found in our country, for lining purposes.

This enamel is also being tested for lining trays employed in the fermentation industry. Cashew enamel does not inhibit the growth of micro-organism especially fungi and there is a possibility of its utilisation as a coating material for fermentation trays as in citric acid production by surface methods.

Cashew shell liquid has been further employed for the modification of rosin for paints and varnishes. By a combined process of esterification and polymerisation of rosin with cashew shell liquid, air-drying varnish resins have been prepared with good weathering properties. The dark colour of the resin, due to cashew shell liquid, can be avoided by employing the distillation product of the shell liquid.

References :

1. Harvey, M. T. and Collaborators: *U. S. Patent* No. 1,795, 791-97, *U. S. P.* 1,977,826. *U. S. P.* 1,828, 071 ; *U. S. P.* 1,821,095.
2. Siddiqui, S. and Azharalikhan : *Indian Patent* No. 28424 (1942).
3. Stadler ; *Annalen*, 1847, **63**, 137.
4. Ruhemaun, & Skinner ; *J. C. S.*, 1887, **51**, 663.
5. Smit ; *Proc. K. Akad. Westenshappen, Amsterdam*. 1931, **34**, 165.
6. Pillay, P. P. : *J. Ind. Chem. Soc.* 1935, **12**, 226.
7. Gokhale, Patel & Shah , *Cur. Sci.* 1949, **9**, 363.
8. Spiegel, L, and Correll, M. *Ber. Deul. Pharm. Ges.* 1913, **23**, 356-78.
9. Spiegel, L., and Dobrin, C., *Ibid.* 1895, **5**, 309-75.
10. Siddiqui, S. & Azharalikhan, *Indian Patent* No. 32237. (1943).
11. Siddiqui, S., Aggarwal, J. S., and Mathur S. K., *Indian Patent* No. 40257.
12. Mathur, H. H., Aggarwall, J. S., and Siddiqui, S., *J. Sci. & Ind. Res.* 1950, **9B** 121—24.
13. Crampton, Farmer and Bemghill, *Jour. of Nutrition*, 1951 **43**, 431-39.

USE OF VEGETABLE OILS IN THE MANUFACTURE OF MODIFIED ALKYD RESINS

BY

OM PRAKASH

Oil Expert to U. P. Government, Kanpur.

Alkyd resins belong to the class of polymers known as polyesters. When a dibasic carboxylic acid reacts with a dihydric alcohol esterification occurs with the liberation of water and linear polyesters are formed, these being the simplest type of alkyd resin. The linear thermoplastic types of alkyds have, however, found little use in industry and the vast majority of commercial alkyd resins are of thermosetting types derived from polyhydric alcohols and polybasic carboxylic acids. The polyhydric alcohol chiefly used is glycerol and the carboxylic acids are phthalic or maleic acids in the form of their anhydrides. The reaction takes place in three stages. The product at first stage is a soluble syrupy liquid but on allowing the reaction to continue, the complexity of the molecule increases and a hard clear resinous material results which is infusible and insoluble in organic solvents. Evidently for surface coatings the insoluble and infusible product is not required, and the course of reaction has to be altered by the use of modifiers so as to give modified alkyds for use in surface coatings. The different modifying agents are fatty oils, natural resins such as rosin, and synthetic resins such as phenol-formaldehyde resins.

The object of the present work was to prepare oil modified air drying alkyds.

1. Linseed oil modified alkyds.

Experiments were carried out by using linseed oil as the modifying agent as follows :—

(a) Linseed oil was heated in presence of 10 per cent glycerine (on the weight of oil) using 1 per cent caustic soda as catalyst to a temperature of 240°C for about $4\frac{1}{2}$ hours. The resulting product was soluble in alcohol. The remaining glycerine and phthalic anhydride were then heated in a separate reactor to form a homogenous solution. The prepared mixture of linseed oil mono and di-glycerides was then gradually added and heated at $180^{\circ}\text{--}200^{\circ}\text{C}$ for 2 to 3 hours. The resin was then transferred to an open basin and heated at 160°C for about 2 hours, till the acid value came down appreciably. Results obtained are given in Table I.

TABLE I.

Expt. No.	Glycerol parts	Phthalic anhydride parts	Linseed oil mono-glycerides, parts	Temperature of reaction °C	Time of reaction hours	Acid value	Nature of the film
1	—	50	100	200	2½	66.2	Tacky
2	—	60	150	230	2	—	—
3	—	45	100	200	2	—	—
4	10	45	50	200	2½	54.8	Tacky
5	10	45	40	200	2½	45.1	Tack Free
6	5	45	50	130-200	2	41.5	„
7	10	35	63	260-265	1½	25	„
8	5	35	50	130-200	2	10	„

Varnishes from Expt. 7 and 8 were prepared and found satisfactory.

(b) The requisite amounts of linseed oil and glycerol were heated together using 1 per cent caustic soda as catalyst for ½ hour to a temperature of 230°C. At the end of this period the two liquids were clear and homogeneous. Phthalic anhydride was then added and the whole mixture heated for 2½ hours at 275°-280°C. Results obtained are shown in Table II.

TABLE II.

Expt. No.	Glycerol parts	Phthalic anhydride parts	Linseed oil, parts	Tem. of reaction, °C	Time of reaction hours	Acid value	Nature of the film
9	50	108	150	275-280	2½	35	tack free but soft
10	55	108	150	275-280	2½	32	„

(c) Another method followed was to heat the requisite amounts of linseed oil and glycerol using 1 per cent caustic soda as catalyst for ½ hour to a temp. of 230°C till a homogeneous mixture

was obtained. Phthalic anhydride was added and the mixture heated till clear. Phosphoric acid was then added and the mixture again heated at 280°C for 2 hours. The object of adding phosphoric acid was to get lighter coloured product, but in our experiments no appreciable decrease in colour was noticed. Results are given in Table III.

TABLE III.

Expt. No.	Glycerol parts	Phthalic anhydride parts	Linseed oil parts	NaOH used parts	Phosphoric acid, parts	Temp. of reaction °C	Time, hours	Acid value	Nature of the film
11	55	108	150	1.7	1.7	280	2	32	tack free but soft
12	60	108	155	1.6	1.8	280	2	—	„

The varnishes prepared from resins from expt. 9 to 12 were not found to be as good as those from Nos. 7 and 8.

2. Castor oil modified alkyds :

Two types of products can be obtained using castor oil :—

(i) Alkyds made at lower temperature :

Here the hydroxyl group in the chain of the oil molecule remains and hence are non-drying in character. These products have considerable application as plasticizing material for nitrocellulose and particularly urea formaldehyde stoving finishes as they have very good colour retention at fairly high stoving temperatures.

(ii) Alkyds made at higher temperature :

Our method was based on the principle whereby during the process of resinification at 265°-270° castor oil was dehydrated. By this process we could obtain air-drying alkyds. In carrying out the dehydration at 265°-270°C, no catalyst was employed as phthalic anhydride itself acts as dehydrating agent.

(a) Glycerol and phthalic anhydride were heated together at 140°C till clear. Castor oil was then added gradually and the whole then dissolved in xylene, solvent distilled off carrying along with it the initial water of reaction. The mixture was then heated to 265°-270°C for 1½ hours to 2 hours. The contents then transferred to an open basin and maintained at 160°C for about 2 hours till the acid value was fairly low. Results are given in Table IV.

TABLE IV.

Expt. No. 1	Glycerol parts 2	Phthalic anhy- dride parts 3	Castor oil parts 4	Temp, of reaction °C 5	Time of reaction hours 6	Acid value 7	Nature of film 8
13	10	45	60	265-270	1½	30.7	Tack free
14	10	35	60	265-270	1½	50	„
15	10	45	60	265-270	1¾	14	„
16	10	30	45	250	1½	36	„
17	10	25	60	265-270	1¾	20	„

Phosphoric acid was also tried in the castor oil product as in method (C) of linseed oil modified resins, and with lime as catalyst instead of caustic soda but no appreciable bleaching of colour was noticed. The sample of varnish prepared in experiment 13 from Table IV above was tested at the Defence Laboratories of the Government of India (T.D.E. L & S) and was reported as under :

General appearance	... Brown coloured, clear and transparent liquid free from sediments.
Visible impurities	... Nil.
Consistency.	... Good.
Application.	... Satisfactory.
Specific Gravity	... 0.97
Surface drying time	... 4 hours.
Hard drying time	... Within 18 hours.
Colour of the varnish film.	... Almost colourless.
Gloss	... Full.
Stripping test.	... Satisfactory.
Webbing	... Satisfactory.
(as per B.S.S. 256,1936)	
Flexibility and Adhesion	... Satisfactory.
(as per B.S.S. 256, 1936)	
Scratch hardness	... Stands 1,000 gms.
(after 7 days drying)	
Flash Point.	... Above 95°F

Volatile Matter,	... 51.9 per cent.
Viscosity at 85°F	... Approx. 2 Poises.
Water absorption	... Nil.
<i>Water vapour.</i>	... Impermeable to water vapour.
Permeability test as per	
J.O.C.C.A. May 1941, Vol.	
XXIV, PP. 122.	

Discussion and Conclusion :

From the above results it was found that with castor oil as modifying agent we obtained light golden yellow coloured resins, which give hard and elastic films. With linseed oil as modifying agent the colour obtained was much darker but the film forming properties were satisfactory. Some experiments were tried with preformed dehydrated castor oil as modifying agent but they resulted in the formation of gel before the reaction was complete.

Some experiments were tried with castor oil as modifying agent without initial removal of water of reaction with solvent (xylene), but the products, obtained in these cases were not satisfactory. It was found preferable to use a solvent (xylene) to assist in the removal of the water of reaction, which also tends to check gelation to a great extent, as also to improve the properties of the resin.

ANALYTICAL AND OTHER
MISCELLANEOUS
PAPERS

ESTIMATION OF A AND B VALUES AND THE BUTYRO REFRACTOMETER VALUE IN THE EVALUATION OF THE PURITY OF GHEE (BUTTER FAT)

BY

DR. N. N. GODBOLE

Director, Industries and Commerce, Rajasthan, Jaipur.

The estimation of purity of butter fat in India has been a very vexed and difficult question. According to the standards laid down by the Government, great importance is attached to R. M. value, Polenske value, acid value, saponification value and refractive index by the Butyro-refractometer. Of these values the refractive index, the R. M. and P. values have received major importance. Even for these the values accepted are average values; scientifically speaking, the averages cannot be taken as the criterion for determining the purity of ghee samples. All these values having variable constants, it is essential that the constants selected should have the least degree of variability. It is proposed that the use of the A & B values would serve this purpose best as the range of variability is the least so far as the B value is concerned. The A value stands for the content of the fatty acid (in a fat) which give rise to water soluble magnesium salts and water insoluble silver salts (saturated acids with 6 to 10 carbon atoms) and the B value is a measure for the content of butyric acid and the next C_5 saturated acid whose magnesium and silver salts are soluble in water. These values are much more reliable than the other values. Work has been done on these values and it is proposed that in the estimation of the purity of butter fat A & B values should receive first importance. In Europe, in the detection of the adulteration of butter by margarine, this value has been used with the best of results. It has been further improved by Grossfeld who has made the experimental work very accurately even with small quantities. The attention of Scientists is drawn to this important question so that this value receives the attention it deserves. Out of all the oils and fats, pure ghee is the only one which contains Butyric acid glyceride and the next higher homologue. The B value indicates the presence of Butyric acid. This is the one constant which is the least variable and, therefore, the detection of this constant should receive the greatest importance.

The methods of determining purity of *ghee* by the Butyro-refractometer has received a great importance. Here also only the averages are given. This is not accurate. The refractometer designed by Carl-Zeiss-Jena is meant for oils and fats within certain ranges. The important feature of this refractometer is a special compensating arrangement in the prisms, whereby dispersion is avoided and a colourless line is obtained between the bright and the shaded parts of the refractometer. In the case of other refractometers such as Abbe's there is the ordinary dispersion and the refractive index is given in absolute numbers. According to the manufactures in the case of pure *ghee* due to the compensation arrangement there should be no dispersion. It has been observed by Godbole and Sadgopal that in the case of Indian samples of *ghee*, in most cases there is always a violet line instead of the colourless spectrum observed between the shaded and the light parts of the refractometer. Godbole and Sadgopal have observed that in the case of adulterated samples where the adulteration is simple, in the line of demarcation, either a bluish green line or a reddish line or an orange red line is observed in the refractometer. Thus they are of opinion that although the refractive index is within the range specified by the standards, yet if the coloured lines (bluish green in case of fats having sap. values 192 to 195) or (orange red line in case of coconut and allied oils having sap. value of 250 or so) are observed, then this is a clear case or proof of adulteration although the other values such as R. M. and P. values may be within the average standards laid down. Further, they are also of opinion that if no colouration is observed in the line of demarcation in the refractometer, no inference should be drawn about the purity of the sample. A number of mixtures of oil have been made with components of *vanaspati*, *Mahawa*, coconut oil, etc. which give the refractive index attributed to pure *ghee* and do not give also any coloured line for demarcation. Therefore special attention should be given to the observation of colour line in the refractometer.

DISCUSSION

Mr. N. S. Bharatia informed that he also found in his experiments on 25 samples of *ghee* that A & B values worked very well for the determination of the purity of *ghee*.

RECENT ADVANCES IN THE ANALYSIS OF OILS AND FATS

BY

DR. S. S. GUPTA

National Chemical Laboratory, Poona.

The rapid advances made in other branches of science, aroused greater interest in the oil chemists for more fundamental work and with better facilities and new experimental technique available, commendable progress was made by workers all over the world. Much more has been accomplished in the past thirty years than in the whole of the preceding century and that is borne out by the rapid strides of progress made in the soap making, edible fats and paint and varnish industries during that period. The fat technologist is no more depending solely on a few common species of vegetable and animal fats. Upto date, more than 500 different varieties of vegetable as well as animal fats have been investigated and their utility for edible as well as industrial purposes explored. Pioneers like Bailey, Hilditch and Jaimeson, and more recently Lovern, Shorland, Longenecker and many others have made valuable contributions to our knowledge and made available innumerable data about the fatty acid composition of all types of natural fats. During the earlier investigations, which were mainly confined to animal tallows and more solid types of vegetable fats, recourse was usually taken to the well known Twichell's lead salt method for separation of the saturated and unsaturated groups of acids. The corresponding methyl esters were fractionally distilled in vacuum and by computing the analytical data of these fractions the final acid composition of the fat was arrived at. Such methods were naturally of little use with the important class of liquid fatty oils, especially the drying oils used by the paint industry, and the highly unsaturated acid of marine animal oils.

During the last decade or so, technique of oil analysis has been revolutionised by the introduction of two newly developed methods. From 1937 to 1942, Brown and co-workers^{1,2} carried on some exhaustive investigations to isolate pure unsaturated acids from natural fatty acid mixtures by crystallisation from common organic solvents at low temperatures. Later, they visualised the usefulness

of the procedure in quantitative investigation of fats and in 1943 the method was employed by Brown and Cramer³ in a component fatty acid analysis of human body fat. The technique has since been further developed and amplified by Hilditch and co-workers^{4,5} and as a result of that, a mass of information regarding the component acids and glycerides of a number of fats, especially of the more complex type, namely, drying oils, marine animal oils, milk fats etc. has appeared from the Liverpool laboratory during the last 5 to 6 years. The method has been useful in segregating these complex acid mixtures into simpler groups which are more amenable to further analysis and thus a more intimate and true picture regarding the composition of these fats is obtained. After many comprehensive studies, it has been found that most efficient and, in many cases, fairly sharp separation is brought about by crystallisation from acetone (usually 10 ml/g). Commencing from the lowest temperature to be employed (generally -60° or -70°C), the deposited acids are later crystallised at higher temperature (-40°C) and, during these operation, the polyethenoid acids are more less completely removed. The residual solids, which are mostly a mixture of saturated and mono-ethenoid acids with traces of the polyethenoid ones, are then crystallised from ether at -26° or -30°C , which brings about a fairly complete resolution of the two groups, comparable to that obtained in the lead salt method. This, in general, has been found to be an appropriate procedure for resolution of fatty acid mixtures from most of the oils. It is, however, open to modification and to suit special circumstances, the temperature, choice of solvent, concentration and time of crystallisation can all be easily varied. This flexibility in itself is a great advantage, apart from the fact that the method involves minimum handling of the highly unsaturated acids and, therefore, chances of oxidation and any structural transformations are largely minimised.

The second important physico-chemical method which is rapidly coming into general use in modern fat analysis is the application of absorption spectroscopy to the estimation and characterisation of conjugated and non-conjugated poly-ethenoid acids. It was again in 1937, the year in which Prof. Brown initiated his important experiments on low temperature crystallisation of fatty acids, that Moore⁶, a biochemist at the Dunn Nutritional Laboratory at Cambridge, noticed that linseed oil acids tended to develop specific absorption bands in the ultra violet spectrum during saponification. He traced this to the action of alkali at high temperature resulting in the practical conversion of pentadiene systems of linoleic and linolenic acids into the conjugated form. This important observation

has since been the subject of critical study and efforts were directed to evolve out the possible use of this phenomenon in the quantitative determination of these unsaturated acids. Mitchell, Kraybill and Zscheile⁷ were the first to propose one such method and recommended an isomerisation of the mixed acids with potassium hydroxide in glycol solution at 180° for 25 minutes, when constant proportions of linoleic and linolenic acids are converted into conjugated diene and triene acids which in turn are estimated by determining the extinction co-efficients at 234 m μ and 268 m μ . Later on, Hilditch, Morton and Riley⁸ put forward a modified method wherein two separate isomerisations 170°/15 min. and 180°/60 min. are conducted for the estimation of triene and diene unsaturation respectively. Spectroscopic absorptions is found to be a linear function and hence the calculations involved are of a very simple nature. Due to its simple operational technique and excellent precision, the method has proved an extremely useful aid to the oil analyst.

Just after the usefulness of 'Low temperature Crystallisation' technique in fatty acid analysis had been established, its application to the study of component glycerides of fats was also investigated and the method was found to be extremely serviceable in that field also. Due to the multiple complexity introduced during the interweaving of fatty acid groups into glyceride molecules, study of component glycerides of natural fats is a very tedious and prolonged affair. Most of the work in this direction has been carried out at the Liverpool Laboratory, where Hilditch⁹⁻¹³ and associates have made some comprehensive studies regarding the glyceride composition of drying oils, butter fat and many land and marine animal oils.

Since the number of mixed glycerides present in these oils is very large and especially since acids of very different character (saturated, mono and poly-ethenoid and all be in combination in single triglyceride molecule), the mutual solubility effect is more pronounced and the resolution of the glycerides presents a lot of difficulty. It is rarely possible to isolate any individual glyceride except in comparatively rare instances when the number of fatty acids present is restricted to 2,3 or at the most 4. Nevertheless, by a careful manipulation of a series of crystallisations, it is practicable to resolve the fat into simpler groups which can be considered as consecutive binary mixtures of the four classes of glycerides; GS₃, GS₂U, GSU₂ and GU₃. Determination of the component fatty acids present in each of these groups permits an approximate estimate of the mixed glycerides therein and thus to obtain similar data for the entire fat.

These important advances in our fundamental knowledge of fats have not only afforded a close insight into the real composition of these complex natural resources, but have also put our soap, paint and other oil industries on a more sound footing. The soap maker is able to know exactly what fatty acids and how much of each should be present in any fat charge he employs and so makes a careful selection of the oils he uses and also knows, how they should be blended to produce best quality soap. Similarly, the exhaustive studies on drying oils have enabled us to define with some exactitude the proportion and arrangement of linoleic and/or linolenic acid groups which are essential in the glyceride of an oil before it is likely to yield a good paint film on exposure to air.

References :

1. Brown and Shinowara ; *J. Amer. Chem. Soc.* 1937, **59**, 6 ; 1938, **60**, 2734.
2. Brown, *Chem. Reviews*, 1941, **29**, 333.
3. Brown and Cramer ; *J. Biol. Chem.* 1943, **151**, 427.
4. Hilditch and Riley, *J. Soc. Chem. Ind.* 1945, **64**, 204, 1946, **65**, 74.
5. Gunstone and Hilditch, *ibid*, 1946, **65**, 8.
6. Moore, *Biochem. J.* 1937, **31**, 138.
7. Mitchell, Kraybill and Zscheile ; *Ind. Eng. Chem. (Anal)*. 1943, **15**, 1.
8. Hilditch, Mortan and Riley, *Analyst*, 1945, **70**, 68.
9. Barker and Hilditch, *J. Oil, Chem. Ass.*, 1950, **33**, 6.
10. Hilditch and Seavell, *ibid*, 1950, **33**, 24.
11. Achaya and Hilditch. *Proc. Roy. Soc.*, 1950, **137B**, 187.
12. Gupta and Hilditch, *Biochem. J.*, 1951, **48**, 137.
13. Gupta, Hilditch and Riley. *J. Sci. Food Agr.* 1951, **2**, 245.

LOW TEMPERATURE CRYSTALLISATION TECHNIQUE

BY

DR. C. B. PATEL *

Department of Industries, Bombay.

J. B. Brown and co-workers^{1,2,3,4} were the first to draw attention to the use of low temperatures in connection with the isolation of pure unsaturated acids. Later on Brown suggested the application of this technique to the separation of natural fatty acid mixtures, because the physical method of crystallization and the low working temperatures have certain advantage over chemical procedures owing to their simplicity and directness. This statement of Brown has later been supported by Hilditch and co-workers⁵.

It will be of interest to indicate the general procedures which have been found applicable especially on vegetable drying oils and some marine animal oils. It should be pointed out here that lead salt separation is desirable in the first instance (prior to low temperature crystallisation) for fats rich in palmitic and stearic acids. However, in case of fats which contain saturated acids less than 20 per cent of the fatty acids the preliminary separations are conveniently done by the crystallisation process. The maximum time of crystallisation may be limited by working conditions to five hours and the operations are usually conducted with 10 per cent solutions of the fatty acids in the solvent.

The following procedure is generally applicable in case of majority of fatty oils. The total fatty acids obtained by hydrolysis of the fatty oil are first crystallised from 10 per cent solution in acetone at -60°C (in some cases at -70°C); the acids left in solution are recovered whilst those deposited may be recrystallised from acetone at -60°C , or in other cases, may then be recrystallised from 10 per cent solution in ether at -40°C . The acids then deposited consist of saturated acids accompanied by small proportions (upto 10 or 20 per cent) of oleic or other mono-ethenoid acids. The acids left in solution in ether at -40°C are mainly those of the mono-ethenoid series, accompanied by some saturated acids and also by

* In the absence of the author, the paper was read by Mr. H. H. Mathur (N. C. L.)

small proportions of linoleic and/or other polyethenoid acids. The greater part of the linoleic acid present, and almost all of the linolenic acid or other poly-ethenoid acids are left in solution in the first crystallisation at -60°C . Owing to the mutual solubility effect small proportions of oleic and saturated acids invariably appear in this group. For this reason the isolation of linolenic acid in its pure form has presented many difficulties.

Hilditch and co-workers⁵ have utilised the low temperature crystallisation technique for the elucidation of component glyceride structure of certain fats, and have further shown that in a mixture of saturated, oleic, linoleic and linolenic acids, the precision of the spectrophotometric analyses is increased if the mixture is first resolved by crystallisation from solvents at low temperature into a series of fractions, in each of which either the saturated, oleic or polyethenoid acids are concentrated.

The separation of saturated acids from a mixture of saturated and unsaturated acids (unsaturated acids containing the same number of carbon atoms in the molecule but differing in unsaturation by one double bond) has presented many difficulties. For example, the separation of oleic, linoleic and linolenic from each other until recently was considered very difficult. An outline of the work carried out by the author in connection with the isolation of pure C_{18} unsaturated acids has been given below to indicate such difficulties.

Before the more recent developments of the low temperature crystallisation and chromatographic adsorption techniques, methods were available for the quantitative determination of fatty acids based on the solubility of their metallic soaps in organic solvents. Amongst these was the method devised by Tsujimoto⁶ who reported the isolation of the highly unsaturated acids from fish oils by the application of lithium salt acetone method. Later, Lovern, Hilditch *et al*⁷ applied the same technique to the separation of the mono-ethylenic from poly-ethylenic acids from many oils of aquatic origin. Based on the above work of Hilditch and co-workers the author attempted to isolate pure linoleic and linolenic acids using the same technique. It was found, however, that lithium linolate and linolenate were insoluble in acetone both cold and hot to give rise to any satisfactory separation from the salts of saturated and oleic acids. Even by using mixed solvents (alcohol and acetone) in various proportions at various temperatures no separation was possible. The author⁸ is of the view that neither the method devised by Tsujimoto nor any modifications of the same would give a high concentrate of linoleic or linolenic acid available hitherto except with the help of low temperature crystallisation technique.

Applying the low temperature crystallisation technique the author isolated pure linoleic acid from three different oils i.e. safflower, sunflower and Niger seed. The first two were chosen for their high content of linoleic acid and absence of linolenic acid. Niger seed was selected even though it contained about 1 per cent linolenic acid because the ratio of oleic to linoleic acid was much less than that of in safflower and sunflower oils. The following observations were made by the author from the above study :

1. The separation of oleic acid from linoleic acid was found to be almost complete in cases where the ratio of oleic and linoleic acids was lowest, even though the actual percentage of linoleic acid in the mixed fatty acids was rather low.

2. From the low temperature crystallisation data obtained on three different vegetable oils it has been concluded that in isolating pure natural linoleic acid two stages are essential.

- (i) In the first stage three or four 10 ml/g. acetone crystallisations (depending upon the weight of mixed fatty acids) initially at -60°C and then at -55°C for five hours are necessary.
- (ii) In the second stage the soluble portions are crystallised a number of times from 20 ml/g. or even more dilute solutions of petroleum at -60°C .

Limitations of the technique :

The application of the crystallisation procedure to the isolation of linolenic acid from the mixed acids of oils rich in linolenic acid — viz. linseed and *conophor* failed to give a pure product. A mixture of a constant composition of approximately 85 per cent linolenic acid and 15 per cent of linoleic acid was obtained which could not be further enriched by crystallisation alone. Thus, the mixed acids (iodine value 215) of *conophor* oil (iodine value 205) left in solution in acetone at -70°C about 80 per cent of fatty acids of Iodine value 242. These crystallised *nine times* from 5 per cent solutions in light petroleum -60°C to -70°C , but the acid separated from the last three crystallisation remained at a practically constant iodine value of 256.

Specimens of approximately pure linolenic acid were, however, obtained by submitting the methyl esters of polyethenoid concentrates of the acid of *conophor* and linseed oils obtained by low temperature crystallisation to separation by chromatographic adsorption technique, employed by Reimenschneider, Herb and Nichols⁹.

Industrial application of the technique:

On the industrial side, Emery Industries Inc. (U. S. A.) in 1934 have developed a pilot plant for the low temperature solvent crystallisation of commercial fatty acids. The separations though non-quantitative have been quite satisfactory from the industrial standpoint. At present commercial units are in operation for the large scale solvent crystallisation of tallow fatty acids to give red oil and stearin. Low temperature solvent crystallised oleic acids, introduced by the Armour Chemical Division¹⁰, are already finding important applications because of their unique combination of properties. Large scale low temperature crystallisation methods have also been evolved for the separation of semi-drying oils, for example Soyabean oil (iodine value 135) yields on fractionation 30 per cent of a paint oil fraction (iodine value 162) and 65.7 per cent of an edible oil fraction (iodine value 125). This procedure, therefore, could very well be employed in case of tobacco seed oil as large quantities of the seeds are available in some of the Indian States.

Data for the large number of edible and non-edible oils as regards their fatty acid compositions are available, however, information as regards the glyceride structure of most of these fats is lacking. India is considered as one of the largest oil producing country in the world abounding in both edible and non-edible oil seeds. There are a number of oilseeds hitherto uninvestigated and special attention is required to the study of these fats. Further no attempts have yet been made for the separation of relatively pure acids on commercial scale from fats by the application of low temperature crystallisation technique.

But the real handicap in applying the low temperature crystallisation technique in India is on account of non-availability of cardice (solid carbon dioxide) to the various research organisations engaged in the preliminary research on oils and fats.

References :

1. Brown & Frankel; *J. Amer. Chem. Soc.* 1941. **63**, 1413.
2. Brown, J. B. & Shinowara, G. Y.; *J. Amer. Chem. Soc.* 1937, **59**, 6.
3. Brown, J. B. & Shinowara, G. Y.; *J. Amer. Chem. Soc.* 1938, **60**, 2734.
4. Brown, J. B. & Stoner, S. G.; *J. Amer. Chem. Soc.* 1937 **59**, 3.
5. Hilditch, T. P. & Riley, J. P.; *J. Soc. Chem. Ind.* 1945, **64**, 204.

6. Tsujimoto, M.; *J. Chem. Ind. Japan*, 1920, **23**, 1000
Chem. Unschan, 1926, **33**, 285.
J. Chem. Ind. Japan. 1923, **26**, 841.
 7. Lovern, J. A.; The Composition of the Depot 'fats of
Aquatic Animals D. S. I. R. Food Investigation Special
Report No. 51 H. M. Stationery Office. London, 1942.
 8. Patel, C. B., Thesis, "Studies of the components of Natural
fatty oils and of methods for their quantitative determi-
nation" University of Liverpool, Liverpool England.
 9. Reimenschneider, R. W. Herb, S. F. and Nichols, P. L.
J. Amer. Oil Chem. Soc. 1949 **26**, 371.
 10. *Chemical and Engineering News*, July 9, 1951 P. 2931.
-

SOME RECENT ADVANCES IN THE STUDY OF THE NATURAL FATS.

BY

DR. A. R. S. KARTHA

Department of Chemistry, Maharaja's College, Ernakulam (S. India).

It has recently been shown by Kartha¹ that the current views on the glyceride composition and metabolism of the natural fats² require considerable revision. The new explanations of the biosynthesis and intermediary metabolism of the fats and fatty acids now suggested¹ have been due to the discovery of the Rule of Glyceride Type Distribution in the natural fats which states that the proportions of the different glyceride types in any fat can be calculated from the saturated acid and fully saturated glyceride contents of the fat by the same calculations irrespective of the component acid composition or biologic source. The discovery of this rule has been due to the development of a new chemical method for estimating the GS_2U as GS_2A^{1a} which eliminates the uncertainties and error involved in the crystallisation procedure. The results from the latter procedure can at best be of only limiting values and it is surprising that though the method has been extensively used and the results obtained given great importance, no instance appears to have been recorded of any attempts at standardising the method, or estimating the probable error involved in a few simple instances using materials of known purity. This evidently ought to have been done before systematic fractional crystallisation studies were started and would have helped in giving the results the importance they deserve.

It would be interesting to trace the progress of the work which has led to the development of the acetic acid-acetone permanganate oxidation of fats and the magnesium salt separation of the azelao-glycerides which together have been responsible for the recent advance in the subject. Following the suggestion in 1927 of the acetone permanganate oxidation method of determining the GS_3 contents of fats, Hilditch and his collaborators investigated for nearly half a dozen years the possibility of making use of the acidic oxidation products in the above reaction for gaining a quantitative insight into the proportions of any one of the non-fully saturated glyceride types and finally gave this up as impracticable in 1933³. During the course

of his investigations, however, Hilditch recorded a number of observations³ which provided the embryonic ideas for further work in this direction.

These ideas are two in number; the first was that GS_2A was insoluble in aqueous bicarbonate wherein all the other acidic oxidation products are soluble; the second was that the magnesium salts of all the azelaoglycerides are insoluble in water. Hilditch and his collaborators had investigated only possible methods for isolating the total azelaoglycerides of any one type in a pure state: Kartha and collaborators⁴ studied the problem in a slightly different way and attempted in the beginning to estimate the proportions of GS_2A in a suitably processed mixture of the oxidation products which will contain all the GS_2A along with some amount of the GS_2A produced, by making use of the first observation namely that GS_2A is insoluble in aqueous bicarbonate wherein all the other acidic oxidation products are soluble. The experimental technique consisted in dissolving the acidic oxidation products in ether and repeatedly shaking this with portions of aqueous bicarbonate under specified conditions⁴ till apparently a mixture consisting of GS_2A and GSA_2 alone was left behind in the ethereal layer. When the above technique was applied by Kartha^{1a} to *Garcinia indica* and *Vateria indica* fats both of which contain about 58-60 per cent of saturated acids and only traces of GS_3 , it was found that the amount of bicarbonate insoluble residue depended largely on the amount of bicarbonate solution used; and that after the major portion of the more acidic products of oxidation was removed in the first two or three shakings, the GS_2A also was seen to be readily dissolved out: these things cannot be readily perceived when working with oils of low saturated acid content of say below about 30 per cent where formerly we could not have had any reasonably correct idea of the minimum proportions of GS_2A produced. Further it was also noted^{1a} that when rather dilute bicarbonate solution was used (2-6 per cent) to minimise the dissolving out of the GS_2A even repeated shakings failed to remove all the nonoic acid as shown by its characteristic smell in the residue. The above experiments which were repeated a number of times divulged another factor also, namely the possible hydrolysis of the GS_2A to GS_2OH during the acetone permanganate oxidation and the possible oxidation of the GS_2OH to other products as well, for when a sufficiently large excess of bicarbonate was used it was found that apart from the amount of bicarbonate insoluble residue being lower than the minimum possible proportions of GS_2A which must have been formed (the weight of the residue was sometimes as low as 40-50 per cent of the weight of the fat) the S.V. of the residual

mono-azelaoglyceride mixture was also considerably lower than the theoretical value for the GS_2A , sometimes by as much as 20-25 per cent.

Naturally before further progress could be made it was necessary to confirm the possibility of the hydrolysis of the azelaoglycerides during the acetone permanganate oxidation under easily and exactly reproducible conditions and it was considered possible that the reported insolubility of the magnesium salts of the azelaoglycerides in cold water could be made use of for this, since Bertram had established in 1925 the ready solubility in water of the magnesium salts of the C_9 and lower mono and dibasic acids produced by the oxidation of the unsaturated acids and this had been confirmed by Hilditch⁵. Hence it was thought that if a fat is oxidised according to the acetone permanganate procedure and the acidic products of oxidation converted to the magnesium salts under specified conditions where all the lower acids will remain in solution as soluble magnesium salts, the amount of fatty matter recovered from the precipitated magnesium salts would give a clear idea as to the extent of hydrolysis involved in the above oxidation procedure.

A *mowhra* oil and groundnut oil (5 gms. each) of known fatty acid composition were hence oxidised by the acetone permanganate procedure, using 9-11 gms. of permanganate per gm. of oil (the total oxidation time being about 9-10 hours) and the total products of oxidation isolated as usual, dissolved in the minimum of carbonate by suspending this in water (50 c. c. per gm. of fat taken) and adding 5 per cent carbonate solution in a thin stream with constant stirring till the solution reacted just alkaline to phenolphthalein. This was then diluted so that a solution volume of 100 c. c. per gm. of fat taken was reached, 30 c. c. of 15 per cent ammonium chloride solution added and then excess of 10 percent magnesium sulphate solution till no further precipitate was formed, the whole procedure being conducted at room temperature. During the Bertram separation for isolation of saturated fatty acids 50 c.c. of solution volume for one gm. of fatty acid mixture is used and in the present instance it was thought that since only the monobasic acids were required to be removed a solution volume of 100 c.c. per gm of fat oxidised would be ample to remove the former at room temperature, since heating the azelaoglyceride salt solutions in the presence of excess of carbonate even for a short time would lead to ready and immediate hydrolysis of the azelaoglycerides. On isolating the azelaoglycerides from the precipitated magnesium salts in the above cases it was found that they amounted only to about 55 and 20 per cent of the fats taken in the two instances whereas had the magnesium salts of all the azela-

glycerides been insoluble as reported in the literature then the azelaoglycerides recovered would have amounted to 70-80 per cent of the fats taken. The magnesium salts remaining dissolved in the filtrates were hence examined when it was found that considerable amounts of the higher fatty acids could be recovered from these showing that either GS_2A or GSA_2 or both gave soluble magnesium salts. The azelaoglycerides precipitated as insoluble magnesium salts were hence analysed for their S content when it was found that it contained from 55-60 per cent of S. showing the presence of large amounts of GS_2A . These results made it appear possible that the Mg salts of GS_2A were only sparingly soluble if not insoluble, whereas the Mg salts of GSA_2 were partially soluble and the Mg salts of GA_3 may be readily soluble under the conditions of precipitation. It was hence considered possible that if a pure GS_2U or GS_3 plus GS_2U mixture is submitted to the above procedure, then more decisive information could be obtained regarding the extent of hydrolysis involved in the oxidation procedure. A mixture of GS_2U plus GS_3 , containing about 33 percent GS_3 was prepared by crystallisation at $30^\circ C$ of a groundnut oil hydrogenated to I. V. about 45 and submitted to the above procedure ^{1a}. The soluble magnesium salts in the filtrate did not contain even a trace of higher saturated acids showing the complete insolubility of GS_2A -Mg salts. The GS_3 plus azelaoglycerides recovered from the filtered precipitates, however, fell considerably short of the quantity theoretically expected. But all the saturated acids in the fat could be recovered from the above mixture. It was hence evident that considerable amounts of the azelaic acid were being split off from the azelaoglycerides during the oxidation since the procedure for the separation of the azelaoglycerides as magnesium salts was far too mild for any hydrolysis of the azelaic acid to take place. It was thus confirmed that hydrolysis of the azelaoglycerides possibly accompanied by oxidation of the hydrolysis products was a factor of considerable importance in the acetone permanganate oxidation of fats.

Further studies showed that acetic acid could be used to eliminate the hydrolysis of the azelaoglycerides involved in the acetone permanganate oxidation without any way affecting the course of the oxidation or the nature of the oxidation products, a quantity of acetic acid enough to combine with all the K in the $KMnO_4$ added being used ^{1a}. The GS_3 plus GS_2U mixture described above as well as a specimen of practically pure distearo-olein prepared by repeated crystallisation from a *Garcinia indica* fat were submitted to the acetic acid acetone permanganate oxidation and the products separated as the magnesium salts when it was found that the amount

of azelaoglycerides recovered agreed well with the theoretical values^{1a}. The absence of any combined fatty acids in the dissolved Mg salts in the filtrates confirmed the insolubility of the GS_2A —Mg salts. To confirm the possibility that no GU_3 is likely to be precipitated as Mg salts under the conditions of separation a specimen of synthetic GU_3 was submitted to the procedure when it was found that no precipitate was produced^{1a}. Hence the azelaoglycerides in the precipitated Mg salts when the above procedure is applied to a fat could be calculated as a mixture of GS_2A on the basis of the S content of the mixture, allowance being of course made for the small quantities of unoxidised GS_2U and the GS_3 , if any, it is likely to contain on the assumption that the S has the same M. M. W. in both the GS_2A and GSA_2 , and that this distribution of the saturated acids actually holds is shown by examination and comparison of the S in the purely GSA_2 fractions separated as soluble Mg salts with that from the GS_2A — GSA_2 fraction separated as insoluble Mg salts, when the two fractions have been found to show approximately the same M.M.Ws. and m.ps. and showed no depression of m.ps. on being mixed. Using this method it was found that distearo-olein added to a specimen of sesame oil could be quantitatively estimated thus establishing the correctness of the method^{1a}. Analysis of mixtures of pure GS_2 and GU_3 not containing any GSU_2 , by the above method, however, showed that in the absence of GSA_2 , certain Mg double salts of GS_2A and GA_3 are precipitated; hence in the analysis of the natural fats the presence of GSA_2 in the soluble Mg salts in the filtrates had to be tested for in order to make sure that the precipitated Mg salts consist entirely of GS_2A alone; when this cannot be demonstrated, the GS_2A estimated may be only minimum limiting values and hence the proportions of GS_2U and GU_3 arrived at may be only minimum limits. It has also been found^{1a} that this precipitation of GS_2A — GA_3 magnesium double salts in the absence of GSA_2 takes place only when the GA_3 in the mixture exceeds about 2-3 per cent, for this much of GA_3 is automatically removed from a mixture containing 3 mols of GS_2A and 1 of GA_3 . It is thus seen that the above method of separation depends upon four factors: (i) the solubility of GA_3 -Mg salts in water under specified conditions; (ii) the insolubility of GS_2A -Mg salts in water under the above condition; (iii) the complete preferential precipitation of GS_2A - GSA_2 -Mg double salts over GS_2A - GA_3 -Mg double salts; (iv) the solubility of GSA_2 - GA_3 -Mg double salts.

The above method of analysis of GS_2U as GS_2A which can evidently be used only in cases where the saturated fatty acids can be isolated by Bertram's procedure has been applied to a series of natural fats and it was these results which showed for the first time

that the glyceride composition of all natural fats is a simple function of the saturated acid and GS_3 contents, the nature of the function remaining entirely unaffected throughout all variations of component acid compositions or biologic source. The esterification of all the natural fats hence appeared to be taking place in the same way, alterations in the proportions of all the glyceride types taking place whenever any regulation of chance distribution was evident in the formation of the fat; these alterations being such that from the value GS_3 chance - - GS_3 actuals, and the chance proportions of the other glyceride types, the actual proportions of all the other glyceride types could be calculated^{1c}. A critical study of the component saturated acid compositions and approximate GS_3 contents of the natural fats^{1d} immediately showed that GS_3 formation appeared to be suppressed in the natural fats as a general feature when the M.M.W. of the saturated acids appeared to go beyond a specified limit for a particular m.p. of fat and hence it appeared that one of the principal results of suppressing GS_3 formation in the natural fats would be the lowering of the m.p. of the fat synthesised in the depots. A study of the course of synthesis and esterification of the natural fats in the depots led automatically to Kartha's hypothesis of esterification^{1a}; this explains not only the glyceride type distribution rule now discovered but also practically every other phenomenon recorded in connection with the glyceride composition of the natural fats.

References:

- (1) Kartha, Studies on the Natural Fats, Vol. I., parts I-III and Vol. II., part IV., published by the author, 1951, Ernakulam.
- (1a) Studies on the Natural Fats, Vol. I., pp 6-29. (1b) Ibid pp 46-48.
- (1c) Ibid, pp 66-72. (1d) Ibid, pp 72-83. (1e) pp 84-110.
- (2) Hilditch, *The Chemical Constitution of the Natural Fats*. 2nd Edition, 1947, Chafman & Hall Ltd., London.
- (3) Hilditch and Saletore, *J. Soc. Chem. Ind.*; 1933, 52, 101T
- (4) Kartha & Menon, *Proc. Ind. Acad. Sci.*; 1943, 17A, 114; 1945, 21A, 228.
- (5) Hilditch and Priestman; *Analyst*, 1931, 56, 354.

CHROMATOGRAPHY IN THE ANALYSIS OF FATTY OILS AND FATTY ACIDS

BY

V. S. GOVINDARAJAN

National Chemical Laboratory, Poona.

As we are well aware the early uses of chromatography in this field were made on the unsaponifiable constituents. Heilborn's work and Drummond's work are very familiar to us all.

Early work by Konda¹⁶, Kaufmann¹⁴, Cassidy² and others showed that fatty acids and glycerides could be separated on a variety of adsorbents such as alumina, charcoal and silica gel. Kaufmann and Wolf¹⁵ separated oleic and elaidic acids by fractional elution from silica gel. Trappe²³ established for lipid constituents the sequence of decreasing adsorption affinities on alumina and silicic acid as follows : phosphatides, fatty acids, cholesterol; tri-glyceride; cholesterol esters; aliphatic hydrocarbons. While these achievements were impressive, it was noted that the separations were only fair and that the reported methods do not allow individual separations within each class. However, these studies revealed the difficulties, some of which are : difficulties of standardizing adsorbents; the considerable reciprocal influence of the individual fatty acids present in the same solution (Cassidy²); the complications in the dependence of adsorption affinity on chain length (e. g. Lauric acid was adsorbed more strongly than stearic acid from light petroleum on certain brands of silica gel or carbon, while other samples showed opposite behaviour).

These earlier investigations were carried out largely by elution analysis or liquid chromatogram procedure. Within the last few years, other methods have been introduced in chromatographic technique. Tiselius²² has given descriptive names for these methods; namely elution analysis, frontal analysis and displacement analysis. Martin and Synge¹⁷ developed a somewhat different method — partition chromatography, which name again is self-explanatory. The development of these methods, the standardization of adsorbents, and the development of the theory and the greater understanding of the factors governing the adsorptions and elutions have resulted in some well defined chromatographic methods in oil analysis. I will deal

with such studies which have been tested fully. For details the individual papers should be referred to and these are mentioned in the excellent reviews by Cassidy and Williams in the "Faraday Society Discussions on 'Chromatographic Analysis'" and the "Biochemical Society Symposia on 'Partition Chromatography'" respectively.

From early studies it was known that separation of free fatty acids from triglycerides could be carried out by adsorbing the acids on alumina. This separation has been standardized by Sylvester, Ainsworth and Hughes²¹. A single passage, of a solution containing triglycerides and free fatty acids in ether, through alumina gives quantitative separation, the acids being adsorbed. This method has obvious advantages over usual method of titration with alkali, as no assumption of molecular weight is made; it is also preferable to the aqueous — alcoholic alkali extraction method which renders possible the inclusion of some lower fatty acid glycerides along with the free acids.

This adsorption method also helps in replacing the lengthy technique of water and alkali washing in the preparation of unsaponifiable matter.

Ideally in elution analysis, the zones are made to march in an ordered array and are recognized by titration or some other method. Though a complete series of such solvent combinations have not yet been worked out, this method is especially applicable to purification of already separated samples. Cassidy demonstrated 0.67 per cent of ester in a sample of mixed acids obtained by careful saponification.

Kaufmann¹⁴ found that both on aluminium oxide and magnesium oxide, the more saturated acids are more strongly adsorbed from light petroleum. Also among the saturated acids, those of higher molecular weights are more strongly adsorbed.

Claesson⁶ developed frontal analysis for the separation of fatty acids and these proceed very successfully, though elaborate apparatus and moderate amount (0.2 — 0.5 g.) of the mixtures were needed. Claesson⁷ reported that by the use of Carboraffin CIV and absolute ethanol, it was possible to obtain quantitative separation of a mixture of 6 fatty acids. A typical example is a mixture of N-C₈, C₉, C₁₀, C₁₂, C₁₄ and C₁₈ acids in the percentages 10, 10, 10, 20, 20 and 30 and the percentages found being 14, 10, 8, 22, 20 and 27.

Holman and Hagdahl^{11a} reported the analysis of a mixture of lauric, myristic, palmitic and stearic acids using picric acid as displacement agent. These authors extended these analyses to the separation of saturated fatty acids from C₁ to C₂₀ and C₂₂^{10a}. A

higher fatty acid was used to displace the mixture of lower acids. Charcoal, Darco G-60 and aqueous ethanol were used. Acids C_1 to C_5 were separated from water with C_6 as the developer; C_6 to C_{20} from 78 per cent ethanol and 22 per cent chloroform with C_{22} as developer. The displacement analysis of saturated, unsaturated and branched chain fatty acids on silica gel has been reported by Claesson^{6a}. Displacement development will not obviously be applicable when substances are adsorbed on different parts of the surface of the adsorbent column. Displacement analysis allows of its use for obtaining substantial amount of components in pure form.

Ramsay and Patterson¹⁹, Elsdén¹⁰, Isherwood¹³, Peterson, Boldingh¹, and others have applied the technique of Partition Chromatography to the analysis of carboxylic acids. From the large number of papers that have been published it appears that this would prove to be a fairly simple and promising analytical technique. Besides the principle of partition chromatography may be applied to columns or paper, thus forming semimicro preparative or purely analytical procedure. The first application of this technique was to the lower fatty acids using silica-water-chloroform or chloroform-butanol systems. Ramsay and Patterson¹⁹ extended these early separation to acid mixtures containing acids upto 19 carbon atoms. For formic to propionic the second solvent was butanol-chloroform; for pentanoic to decanoic, methanol is the supported phase and 2:2:4 trimethyl pentane as the mobile phase; for hendecanoic to nonadecanoic, furfuryl-alcohol and 2-amino pyridine formed the supported phase and hexane the mobile phase.

Reversed phase techniques have been developed by Boldingh¹ and Howard and Martin¹² for the analysis of higher fatty acids. Boldingh¹ successfully separated methyl esters of long chain fatty acids on filter paper impregnated with vulcanized rubber latex and column of the same. Howard and Martin¹² used keisulghur treated with dichloro-dimethylsilane vapour, thus making it 'unwettable' by strongly polar solvents. These carriers successfully retain the less polar phase of numerous solvent systems, e.g. paraffin or a paraffin-aqueous acetone mixture; solvents like paraffines; aromatics, chloroform, etc., with methanol-acetone mixture as mobile phase.

Boldingh¹ using column of 15-18 x 1.2 cm. determined quantitatively to within a few per cent a mixture of 2-10 mg. of C_6 to C_{18} acids. A vulcanized rubber powder - 'Mealorub' partly swollen with benzene and equilibrated with the mobile phase consisting of a mixture of polar organic solvents methanol and acetone (3:1 v/v) with water was used. The water content of the mobile phase was reduced for the separation of the higher acids. When unsaturated

acids are present there is disturbance in the ordered picture obtained with saturated acids. Oleic elutes between palmitic and stearic acids while linoleic ran as fast as oleic and linolenic faster. Since stearic acid is fully separated from unsaturated acids, it is suggested that analysis before and after being fully hydrogenated, combined with diene and triene determinations will give a full picture of C_{16} — C_{18} acids. Hydroxy fatty acids like ricinoleic acid was found to run faster than other fatty acids, with a mixture of 70 parts methanol and 30 parts of water and this affords a simple method, of estimation of hydroxy acid content of fats and oils, provided saturated acids lower than C_{12} are absent. A castor oil containing 85 per cent ricinoleic as determined by hydroxyl value gave 82.5 per cent of ricinoleic acid by chromatographic method. Howard and Martin¹² have reported similar results using treated keisulghur and aqueous acetone-paraffin, the recovery being 95–100 per cent. Besides they found that with constant chain length, increasing the degree of unsaturation increases the rate of movement down the column, The hydroxy acids, ricinoleic and dlhydroxy stearic acids, travel very quickly down the column and are completely separated from saturated and unsaturated acids. Thus the interesting observation is made that the saturated and unsaturated acids could be readily separated by oxidizing the mixture before chromatography.

The separation of mixtures of homologous carboxylic acids into their components is difficult. The difficulty is greater as the amount of mixture available is smaller and complex as encountered in biochemical experiments. In these respects the chromatographic methods seem to offer elegant solutions.

Early studies showed that monoglycerides are more strongly adsorbed by alumina than are diglycerides, and the diglycerides more than triglycerides. Walker and Mills²⁴ succeeded in separating linseed oil into fractions containing 7, 6, 5 and 4 double bonds per molecule by repeated fractionation on aluminium oxide from *n*-hexane. Thus one fraction would contain mono-oleo-di-linolenin and dilinoleo-monolinolenin both with 7 double bonds: a second would include tri-linolein, oleo-linoleo-linolenin, mono-saturated-dilinolenin each containing 6 double bonds and so on. The constituents of the oil were found to range themselves in the decreasing order of unsaturation. Dutton's⁹ study on separation of ethyl stearate, oleate, linoleate and linolenate on alumina using solvent containing 1.75 per cent diethylether in petroleum (under nitrogen pressure) showed that best separation was obtained in stearate-linolenate system where there is greatest difference in unsaturation. The systems with small difference in unsaturation are poorly separated. Reinbold and

Dutton²⁰ studied the fractionation of soybean oil on aluminium oxide and developing with 35 per cent diethylether in petroleum ether. The percentage composition of fatty acids in each fraction was calculated from spectrophotometric determinations and iodine value. They report that the method compared favourably with other methods, the iodine value of the fractions ranging from 104 to 173, a spread of 69 units. Recoveries from the column were 82.4 per cent with glycerides.

I will close this review by mentioning the use of chromatography in some specific determinations. The methods available so far, for estimation of oxidized acids depend on the precipitation of oxidized acids from normal acids in light petroleum. Since the normal acids have a solubilizing effect on the oxidized acids, errors are introduced. Williams²⁵ used adsorption on calcium carbonate to strip the petrol solutions of traces of oxidised acids. These are then eluted with ether and added to the main precipitate of oxidised acids. Dugan and Coworkers⁸ used chromatography to study the peroxidic compounds resulting from autoxidation of methyl linoleate. They used sodium aluminium silicate and *iso*-octane. The ester were reduced from 1003 PV (peroxide value) to 28 PV by passage through column and obtained fractions ranging in PV from 28 to 2790.

Lastly the estimation of small quantities of hydro-carbon in oils has been mainly possible by chromatography. Typical instances are the determination of squalene in olive oil, wheatgerm oil, rice bran oil and the direct separation of mineral oil from wool grease, linseed oil, and rapeseed oil. Williams²⁵ has shown that by chromatography of the unsaponifiable matter, hydrocarbons in excess of about 0.1 per cent may be completely separated and determined. An important application of chromatographic technique is to prepare component acids in pure state. A typical example of this is the preparation of pure linolenic acid of over 98 per cent purity by the techniques of low temperature crystallization and chromatography on silica gel¹¹.

Chromatography has been used for three purposes:

(1) as an analytical tool which gives information about how many and which component are present in a mixture; (2) how much of each is there; and (3) as a preparative tool for obtaining components of a mixture in a pure form.

References:

1. Boldingh, *Rec. Trav. Chim.*, 1950, **69**, 247.
2. Cassidy, *J. Amer. Chem. Soc.*, 1940, **62**, 3073, 3076.
3. Idem, *Ibid*, 1941, **63**, 2735.

4. Idem, *Federation Proceedings*, 1948, **7**, 464.
5. Cassidy and Williams, *Faraday Society Discussions*, 1949, No. **7**, 259.
6. Claesson, *Arkly. Kem. Mineral. Geol.*, 1946, **23:A:1**, 1.
6A. Claesson; *Rec. Trav. Chim.*, 1946, **65**, 571.
7. Claesson; *Ann. N.Y. Acad. Sci.*, 1948, **49**, 183.
8. Duggan *et al*, *J. Amer. Oil Chem. Soc.*, 1948, **25**, 153.
9. Dutton and Reinbold, *J. Amer. Oil Chem. Soc.*, 1948 **25**, 120.
10. Elsdon, *Biochem. J.*, 1946, **40**, 252.
- 10a. Hagdhal and Holman, *J. Amer. Chem. Soc.*, 1950, **72**, 101.
11. Hilditch, Patel and Riley, *Analyst*, 1951, **76**, 83.
- 11a. Holman and Hagdhal; *Arch Biochem.* 1948, **17**, 301.
12. Howard and Martin; *Biochem. J.*, 1950, **46**, 532.
13. Isherwood, *Biochem. J.*; 1946, **40**, 688.
14. Kaufmann, *Fette u. Seifen*. 1935, **46**, 268 and later papers.
Angew. Chem., 1940, **53**, 98.
15. Kaufmann and Wolf; *Fette u. Seifen*, 1943, **50**, 519.
16. Kondo; *Pharm. Soc. Japan, Trans.*, 1937, **57**, 218.
17. Martin and Synge; *Biochem. J.*, 1941, **35**, 1358.
18. Peterson and Johnson; *J. Biol. Chem.*, 1948, **174**, 775.
19. Ramsay and Patterson; *J. Assoc. Off. Agri. Chem.*, 1945, **28**, 644; 1948, **31**, 139, 164, 441.
20. Reinbold and Dutton; *J. Amer. Oil Chem. Soc.*, 1948, **35**, 117.
21. Sylvester *et al*; *Analyst*, 1945, **70**, 295.
22. Tiselius, *Advances in Colloid Sci.* (Interscience, New York) 1942, P. 81.
23. Trappe; *Biochem. z.*, 1940, **306**, 316.
24. Walker and Mills; *J. Soc. Chem. Ind.*, 1942, **61**, 125; 1943 **62**, 106.
25. Williams; *Analyst*, 1936, **71**, 259.
26. Williams; *J. Assoc. Off. Agric. Chem.* 1949, **32**, 608.

STABILISATION OF EDIBLE FATS

BY

S. C. SETHI

National Chemical Laboratory, Poona.

A study of the compounds which can be good antioxidants for oils and fats was initiated by Moureu and Dufraisse¹ in 1922, who observed that certain phenolic compounds like hydroquinone and pyrogallol can prevent auto-oxidation. But it is essential that the anti-oxidants for edible fats must be safe pharmacologically, non-toxic, fat soluble and should not affect the odour, taste and color of the oil.

Various workers tried to isolate natural antioxidants from the crude vegetable oils and use them for the fortification of fatty oils. Thus, sesamol from sesame oil, gossypol from cottonseed oil and lecithin and tocopherols from other oils are found to be very effective antioxidants. Besides this, the wheat germ oil itself is a good stabilizer for oils; squalene from the unsaponifiable matter of shark liver oil, is also supposed to have the same properties.

Gisvold et al and Blaizot and Cuvier² found nor-dihydroguaiaretic acid to be an excellent antioxidant for animal and vegetable oils and a good stabilizer for carotene and vitamin A of the oils. 0.003 per cent of N. D. G. A. is enough to stabilize lard for a year, according to Sandell and Spross³.

Other important antioxidants for edible fats include: (1) gallic acid and its esters - very good for lard and vegetable shortenings, peanut and cod liver oils; Lea⁴ found that .005 per cent of ethyl gallate considerably retarded the development of tallowy odour in butter fat stored at 37°C; ethyl gallate or *iso*-butyl gallate together with synergists have been reported by Bose⁵ to have beneficial effects on the stabilization of vitamin A in shark liver oils. (2) Dugon⁶ observed that butylated-hydroxy anisole (3-*ter*-butyl-4-hydroxy anisole) when used alone or with synergists, was effective for lard and frying oils viz., corn oil, groundnut oil and also foods prepared from these; and simultaneously delays the vitamin losses. (3) Citric acid - (.005 to .05 per cent) acts both as a metal de-activator and synergist as reported by Lemon and coworkers.⁷ (4) Glycerol monogallate-dipalmitate was found to be most effective for fish oils

by Bittenbender.⁸ (5) Benzoin, gum guaiac, ascorbyl ester, oatmeal powder, and a mixture of tocopherols and vitamin B complex are among the various other antioxidants recommended.

Various antioxidants which are very effective for butter stored at room temperature, according to Swartling⁹ and Reinart¹⁰ are gallic acid esters, N.D.G.A. and hydrocaffeate esters.

In 1947, Kolyeareas¹¹ found that the alcoholic extract of anis seed was very good for the preservation of olive oil. He also worked with mustard seed extract, but this was not very effective. Dhar and Aggarwal¹², in the mean while, observed that wheat-germ oil and Kamala dye together with synergists are very good stabilizers for *ghee* and vegetable shortening. They also tried the alcoholic extract of anis seed for this purpose and found that it was good for the preservation of *ghee*.

Since very early times in India, it has been customary to add a few spices or condiments to the vegetable oils and *ghee* before storing them. The most common of these materials are red chillies and betel leaves. With a view to study the scientific aspects of this practice, work was started recently at the National Chemical Laboratory, Poona. About 24 common spices and condiments were selected for this purpose, and almost all the popular edible vegetable oils of India and butter fat were subjected to these tests.

This various refined oils were heated to 220°C with definite amounts of the spices, and after filtration, were subjected to the modified 'Swift Stability test' at 97.7°C for 5 hours. The peroxide and acid values of these treated oils were compared with those of original oils and similarly heated oils without the addition of spices, all being submitted to the oxidation test. The results obtained show that the initial heating of the oil decomposes some of the peroxides. These are in harmony with the observation of Triebold¹³, who noticed that good keeping quality crackers could be produced from shortening showing poor keeping qualities, which he thought is due to the destroying of the pro-oxygens in the processing of the crackers. The results also show the ease with which the antioxidant principles are extrated from these materials by heat alone. They also indicate that even at such high temperatures, which are actually the temperatures of frying the antioxidant principles of the spices are not destroyed.

The oils subjected to these tests were groundnut, safflower, sesame, mustard and coconut oils and *ghee*. Some of the results are given below :—

Spices or Condiments and treatment.	Peroxide Value.	Spices or Condiments and treatment.	Peroxide Value.
Groundnut oil:		Mustard oil:	
Original oil aerated	100.5	Original oil aerated	20.6
" " heated and aerated.	76.9	" " " after heating	15.1
Betel leaves — 2%	6.2	Red chillies — .5%	10.1
Red chillies — .5%	23.4	1.5%	3.3
1.5%	7.1	Pepper — .5%	14.9
Cinnamon leaves — .5%	12.8	1.5%	3.4
1.5%	7.5	Cloves — .5%	9.1
Turmeric — .5%	25.2	1.5%	4.5
1.5%	9.5	Dry ginger — .5%	7.6
Dry ginger — .5%	19.8	1.5%	4.7
1.5%	9.9		
Safflower oil:		Coconut oil:	
Original oil aerated	362.2	Original oil aerated	51.0
" " heated and aerated	222.8	" " heated and aerated	35.1
Turmeric — 1%	33.8	Turmeric — .5%	4.4
2%	27.1	1.5%	2.7
Cloves — 1%	33.7	Dry ginger — .5%	8.3
2%	20.4	1.5%	3.5
Nutmeg mace — 1%	43.9	Betel leaves 2%	7.8
2%	25.3	Green ginger 2%	21.7
Nutmeg fruit — 1%	74.7		
2%	27.8		
Pepper — 1%	105.8		
2%	27.9		
Sesame oil:		<i>Ghee</i> (Butter fat):	
Original oil aerated	396.6	Original oil aerated	99.4
" " heated and aerated	198.0	" " heated and aerated	103.3
Cloves — .5%	15.8	Cloves — .5%	3.8
1.5%	3.1	1.5%	1.7
Red chillies — .5%	102.6	Red chillies — .5%	42.1
1.5%	8.7	1.5%	3.0
Turmeric — .5%	78.0	Betel leaves — 2%	6.8
1.5%	8.7	Nutmeg fruit — .5%	23.8
Green chillies — 2%	28.8	1.5%	5.8

Thus, it can be observed that these spices are quite effective in the preservation of the foresaid edible oils. The most effective of these spices as found out by Sethi and Aggarwal¹⁴, are red chillies, cinnamon leaves, turmeric, cloves, pepper, nutmeg fruit, betel leaves and dry ginger.

A further support, on the effectiveness of these spices, is furnished by the actual keeping test of the treated and untreated oils, for a period of 6 months, which are also in the same line.

It may be mentioned here, that all these results are obtained by using the powdered spices as a whole, and it seems to be quite evident that if the active principles of these spices are extracted and used for the stabilization of fats, the effectiveness will be much enhanced and the percentage required greatly reduced. Work on these lines is in progress at the National Chemical Laboratory, Poona.

References :

1. Moureu and Dufraisse; *Compt. Rend. Soc. Biol.*, 1922, 86, 321.
2. Blaizot & Cuvier ; *Oleagineux*; 1950, 5, 164—6.
3. Sandell & Spross; *Svensk, Farm. Tid*, 1950, 54, 61.
4. Lea ; *J. Soc. Chem. Ind.*, 1944, 63, 107.
5. Bose ; *Current Science*, 1947, 16, 119.
6. Dugon, *et al* ; *Food Technology*, 1950, 4, 457.
7. Lemon *et al* ; *Can. J. Res.* 1950, 28F, 453.
8. Bittenbender; *Can. Fisheries Rev.*, 1950, 12, No. 2.
9. Swartling; *Proc. Twelfth Internat. Dairy Congress*, 2, 375.
10. Reinart; *Proc. Twelfth Internat. Dairy Congress*; 2, 405.
11. Kolyeareas ; *J. Am. Oil. Chem. Soc.*, 1947, 24, 39.
12. Dhar & Aggarwal: *J. Sci. & Ind. Res. (India)*, 1949, 8, 1-4.
13. Triebold; *Oil and Soap*, 1945, 22, 334.
14. Sethi, S. C. and Aggarwal, J. S. ; *Nature*; 1950. 166, 518.

DISCUSSION

Dr. S. A. Saletore apprehended that spices on account of their smell and taste might not be good antioxidants. Moreover, peroxide value although quite useful would not indicate the exact stage of rancidity of various oils and fats. Taste and smell which are the only reliable indications of rancidity would be masked by spices and condiments.

Mr. T. M. Vishram while considering the importance of the work on stabilization of edible fats thought that on account of high

prices of spices and condiments, it might not be possible to use them for such purposes. He suggested that some cheap herbs might be tried for stabilization of edible fats.

Mr. V. D. Mariwala, Vice President, The Oil Merchants Chamber asked whether black pepper had been tried for the preservation of edible fats because this was being used in America for the preservation of different types of food.

Mr. S. C. Sethi informed that the amount of spices used was not much and so their colour, taste and smell would not be perceptible in oils and fats. They are, moreover, non-toxic substances. The prices of everything was high but even then substances like onions, garlic, betel leaves were quite cheap and might stabilize the fats satisfactorily. As regards black pepper, it was found as one of the best stabilizers.

Dr. J. S. Aggarwal while supporting the statements of Mr. Sethi, informed that 1-1.5 per cent of the spices that were being used at that time might still further be reduced to much less amount and it required further experiments to establish the least quantity required for stabilising purposes. Moreover, experiments were in progress to find out the antioxidant effects of some herbs. As reported betel leaves had proved quite effective antioxidant and was a very cheap material.

ESTIMATION OF ACETYL VALUE IN DETERMINING THE RANCIDITY OF OILS AND FATS

BY

DR. N. N. GODBOLE

Director, Industries & Commerce, Rajasthan, Jaipur.

The question of the determination of rancidity of oils and fats is a very complicated one, and a good deal of work is being done on the different methods of determining rancidity. While working on the various factors causing rancidity of butter fat such as action of light, air, moisture, nature of the container, etc. it was incidentally found that when acid rancidity sets in the glyceride molecules get attacked and the acid radicals in the glyceride molecules are replaced by the OH molecules. This was carefully examined and it was found that with increase of time and rancidity, the acetyl value was also similarly affected. As is well known ordinarily the acetyl value is a characteristic of OH groups present in oil like castor oil (ricinoleic acid). Therefore, old samples of *ghee* were collected and the acetyl values of these was examined. It was found that the acetyl value went on increasing with an increase in rancidity. Full work was done on the rancidity of *ghee* so far as this value is concerned. It is suggested that the determination of this value should be taken up as one of the factors in determining the rancidity of oils and fats in general to find out how far the acetyl value would be a criterion for determining rancidity.

APPLICATION OF ELECTRICAL TESTING METHODS IN THE PROCESSING OF OILS

BY

DR. B. R. Y. IYENGAR

National Chemical Laboratory, Poona.

Generally the chemical methods of analysis like the determination of iodine number, acid number and physical constants like refractive index and viscosity are employed to serve as guides in following the changes that occur when a drying oil is being processed or reacted. Owing to their elegance, accuracy, reproducibility and simplicity of operation the physical methods are becoming more popular. It is the purpose of this paper to elucidate the usefulness of a comparatively recently developed physical technique, viz. the measurement of dielectric constant, in the drying oil field.

During the processing of drying oils, one is often confronted with the problem of distinguishing by analytical methods, the process of heat bodying from oxidation. The common methods of chemical and physical analysis do not provide the answer to this. Thus in the case of linseed oil, to quote only an example, the iodine value fails with the progress of polymerisation, as also of oxidation. Similarly refractive index, molecular weight (freezing point depression method) and viscosity register a gradual increase in both cases. The problem, however, lends itself to solution by the application of the electrical testing method referred to earlier.

It is well known that dielectric constant is a property which is sensitive to the presence or otherwise of unsymmetrically arranged polar groups in a molecule. Since oxidation or 'blowing' involves the addition of oxygen, and hence the introduction of a polar group in the molecule, oxidised oils may be expected to differ from polymerised oils as far as electrical properties are concerned. This surmise was confirmed by the investigations of Hazlehurst² and O'Hare *et al*³ on the electrical properties of linseed oil. It was found that the static dielectric constant rapidly increased as oxidation progressed whereas heat polymerisation did not have any effect on this property. Further Hazlehurst's studies indicated that the slopes of the dielectric constant temperature curves were characteristic of the conditions of oxidation. Thus the dielectric constant was not

only a measure of the *degree* of oxidation but also an indication of the *nature* of the methods of oxidation.

The preliminary investigations on dehydrated castor oil conducted by the author at the Indian Institute of Science, Bangalore indicated that the dielectric constant may be employed as a measure of the degree of dehydration. Here again, the elimination of the polar OH group during dehydration, from the ricinoleate molecule is responsible for the difference in the electrical properties between castor oil and dehydrated castor oil.

The application of dielectric constant studies is not limited merely to the field of drying oils, but can as well be extended to the case of other industrially important varnish constituents. Investigations conducted by the author¹ on commercial samples of cashew nut shell liquid revealed that each sample is characterised by its dielectric behaviour depending upon: (i) viscosity which is influenced by the nature and extent of polymerised products present, (ii) its content of anacardol. Since these two factors have an indirect bearing on the source of the shells and method of extraction of the commercial oils from the shells it is obvious that a simple technique like the measurement of dielectric constants could be very helpful for standardizing the conditions for plant processing in industrial practice.

The illustrations cited above bear ample testimony to the fact the study of the dielectric properties provides the oil chemist with a powerful tool in his endeavour to solve the numerous problems in plant process control with which he is often confronted.

References :

1. Iyengar and Krishnamurthy; *Ind. J. Phys.* 1950, **24**, 23.
2. Hazlehurst; *Paint Manfr*; 1943, **13**, 275, 302.
3. O'Hare, Hess, and Kopacki; *J. Am. Oil. Chem. Soc.*, 1949, **26**, 484.

DISCUSSION

Dr. K. K. Dole wanted to know from Dr. Iyengar the experimental data on di-electric constant of dehydrated castor oil.

Dr. Iyengar, informed that as only preliminary experiments in this direction were undertaken at the Indian Institute of Science, Bangalore, the full data could not be reported.

CARILLA SEED OIL GEL

BY

DR. J. W. AIRAN

Wilson College, Bombay.

Carilla Plant (*Momordica charantia*, N. O. Cucurbitaceae) is called *Karela* in Hindi, and *Karla* in Marathi.

Villagers usually grow these creepers round the fringe of their fields and cane-sugar plantations. No special care seems to be necessary during the period of their growth. There are some more varieties of this plant.

M. Charantia seeds yield nearly 35 per cent oil by solvent extraction, on the weight of decorticated seeds.

Three important observations about this oil have been noticed:—

1. The oil contains only one saturated acid, viz. stearic acid which is 17 per cent of the total acids.
2. The oil undergoes polymerisation on standing, and much more quickly on exposure to air. The product obtained is a yellowish white solid which can be converted into powder by merely crushing it between fingers. If the oil is spread in a layer, the surface develops wrinkles.
3. This polymerised product then changes to a highly viscous liquid, reddish in colour, and becomes transparent on further standing and without the addition of any other material to it. This conversion can be hastened by autoclaving the polymerised powder. But the green tinge which it now shows would disappear only after a few days.

The unsaturated fatty acids so far identified are oleic and linoleic acids. But it is felt that one other unsaturated acid remains to be identified. The very rapid manner in which the oil undergoes transformation, and the failure of the Wijs method for iodine value determination have added to the difficulties in handling the oil.

Investigations so far carried out of the oils from the seeds of the various species belonging to the natural order cucurbitaceae have shown linoleic, oleic, palmitic and stearic acids as the major components forming their glycerides. Instances have, however, been found in which presence of other acids (α -elaeostearic in *Telfairia occidentalis*; linoleic in *T. pedata*; and trichosanic acid in *Trichosanthes cucumeroides*) have been detected.

It is already known that oils containing elaeostearic glycerides, and the acid itself or its esters possess the characteristic property of gelation when submitted to the action of heat.

Since addition of benzene and alcohol extracts of the seed shells delayed polymerisation of the oil, it is planned to extract the undecorticated seeds with various solvents. The decorticated seeds will be extracted separately and antioxidants like hydroquinone, ethyl gallate and NDGA will be added to the extracted oil.

To eliminate any effect of heat either *ghani* extraction will, have to be tried or cold extraction with petroleum ether, b. p. 40°C, would have to be resorted to.

It is expected that a resin may be present which polymerises on its extraction from the natural cell. This resin may have a catalytic effect in polymerisation.

Preliminary, experiments carried out by the author indicate the possibility of the use of *carilla* oil to induce polymerisation in certain oils.

INFORMATION

Dr. J. S. Aggarwal informed that in the N. C. L. they had carried out research work on the analysis of the seed oils from *Trichosanthes anguina* (*Chachinda*) and *Trichosanthes dioica* (*Palwal*) which plants also belong to the same natural order, (Cucurbitaceae) as *carilla*. In both cases a conjugated triene acid was isolated. It could easily be separated due to its insolubility in petrol ether especially after irradiation in ultraviolet light in presence of traces of iodine. In the case of *Carilla* oil fatty acids he could also separate an acid having similar properties by the method mentioned above. In his opinion the gelation of the oil was due to the presence of the conjugated acid. But as the acid in the oil might not be more than 15-20 per cent, the nongelled portion of the oil would dissolve the soft gel that was formed. That might explain the reconversion of the gel into liquid again. In the case of tung oil and Kamala oil, the conjugated acids are more than 50 percent of the total acids. So the gels were comparatively harder and could not again change to liquid state.

VEGETABLE OILS AS PETROLEUM PRODUCTS SUBSTITUTES

BY

DR. MOHAN LAL KHANNA*

National Physical Laboratory, New Delhi.

Whenever estimates of world's petroleum resources have been made, fears have invariably been expressed that the oil reserves cannot indefinitely cope with an ever increasing demand for petroleum products and that a world shortage will make itself felt in the course of time. As far back as 1911, Rudulf Diesel, the inventor¹ of Diesel engines visualized that when resources of mineral oil become depleted, the sun's radiant energy will still be available to produce vegetable oils from the soil for use in Diesel engine. It is also not surprising to find that countries like U. S. A. and Canada, which are self-sufficient in petrol and petroleum products, have recently been engaged in the development of petrol substitutes at their national laboratories². It is a matter of utmost certainty that every nation in the world should either be self-sufficient in her natural resources of mineral oil or must proceed towards seeking artificial means of producing the same or otherwise look for substitutes. The output of Indian oil fields is inadequate. Most of her requirements are being fulfilled through imports. The total quantities of mineral lubricating oils and greases³ imported during 1949-50 were 40 million imperial gallons and 5.5 million lbs respectively valued at nearly seven and a half crores of rupees.

It is now known that vegetable oils can be used both as Diesel fuels and lubricants. This country ranks at present as one of the major oil-seed producing areas in the world. It was, therefore, felt desirable to undertake a brief survey of the past work done on the use of Indian vegetable oils as petroleum products substitutes and also to indicate the new lines on which future research work could be carried out beneficially.

Motor Spirits : It is not possible to burn vegetable oils as such in the petrol engine, unless oil molecules are split up into simpler molecules by thermal cracking. This has been studied by many

* In the absence of the author an abstract of the paper was read by Mr. A. S. Gupta (N. C. L.)

workers earlier, notably by Kobayshi⁴, Saito⁵, Maihle⁶, Waterman and Perquin⁷, Haga⁸, Egloff and Morrel⁹, etc. Cracking the soap of vegetable oil or the oil itself alone or catalytically decomposes fatty acids into hydrocarbons. Subsequent cracking of these hydrocarbons is somewhat similar to petroleum cracking. During the war, industrial batch-cracking process was developed in China to produce motor fuels from vegetable oils. Tung oil served as the main raw material. The experimental methods adopted for the preparation of crude oil roughly fall into (a) destructive distillation of vegetable oil and the simultaneous or subsequent cracking of its vapour, (b) liquid-phase cracking of vegetable oils with or without catalysts and (c) pyrolysis of the soaps of vegetable oils. Various other oils tried were rapeseed, soybean and cotton-seed. The technical aspects of the process are described by Chang and Wan¹⁰.

Laboratory scale experiments on the thermal cracking of groundnut and *Mowha* oils under pressure in an autoclave and in a long vertical tube with and without the use of metallic salts as catalysts, were performed in India by Dalal and Mehta¹¹. Thermal cracking of vegetable oils by the non-residue method of distillation under pressure at 300 lbs per square inch was extended in the same laboratory to other vegetable oils by Mandlekar, Mehta, Parekh and Thosar¹¹. Further studies with a view to obtain an optimum yield of motor fuel fraction and engine trials with its use are called for.

Investigations to obtain the optimum yield of sebacic acid¹ from castor oil and the destructive distillation of vegetable oil soaps¹ were also conducted in the Laboratories of C. S. I. R.

Another way of achieving the same end is to provide a small but compact cracking unit on the transport vehicle. Attempts in this direction were made by Apte¹⁴. In this case groundnut oil could easily be replaced by crank-case drained oil collected in a garage or a cheaper oil. Though serious attention has been given to locate new reserves¹⁵ of mineral oil, to manufacture synthetic petrol by the Fischer-Tropsch process from the existing grades of Indian coals¹⁶ and to process Arabian imported crude oil in a refinery plant at Bombay¹⁷, yet attempts to manufacture motor spirits by thermal cracking of Indian vegetable oils also deserve an equal attention.

Diesel Fuel: In the laboratories of the C.S.I.R., Aggarwal, Chaudhury, Mukerji and Verman¹⁸ demonstrated that most of the Indian vegetable oils could be successfully employed as Diesel fuels. Some of them could be used without any modification in the engine while others required the use of corrosion-resistant alloys engine parts. In comparison with mineral oils, vegetable oils, in general,

gave approximately the same power output, a slight high fuel consumption, better brake thermal efficiency and slightly more carbon deposits in the combustion chamber. Cotton-seed oil, in particular, gave exceptional performance in that its consumption was definitely less than that of the mineral oils. Powdered fuels as such have also been tried as Diesel fuels in other countries but they require engines of altogether different design¹⁹. Colloidal fuels²⁰ containing low-ash charcoal dispersed in groundnut oil were prepared. With the use of stabilizer prepared out of the oil itself, colloidal fuels containing as high as 35 per cent by weight of charcoal could be obtained. It was found that their thermal efficiencies approach that of groundnut oil and that the charcoal part of the fuel could be burnt as effectively as the oil itself. The major defect was that the injection system could not stand up to the abrasive action of the colloidal fuel.

The present engines are primarily meant to use mineral oils. It is most likely that the study of combustion mechanism of these fuels inside the engine cylinder might lead us to modify certain engine parts so that it is possible to burn these fuels most efficiently.

Engine Lubricants: Long before the discovery of crude mineral oils, animal and vegetable oils and fats have been used as lubricants. Though with the enormous success of petroleum lubricants, vegetable oils have now been almost completely replaced, yet vegetable oils have still to be mixed with petroleum products so as to impart certain characteristic properties, which are otherwise not present in the mineral lubricant. Bhatnagar²¹ pointed out that fatty acid molecules of vegetable oils possess oiliness to a remarkable extent. Hardy²² observed that the addition of small amounts of fatty acids to mineral oils gave a considerable amount of reduction in the coefficient of friction and esters with high molecular weight were better lubricants than the lower esters of fatty acids and glycerine. Later independent investigations by Langmuir²³, Adam²⁴ and Hardy²² have revealed that monomolecular adsorption of fatty acids on metallic surfaces reduces the coefficient of friction to a considerable extent and protects the surface from wear and seizure. The adherent thin film of oil on the surface plays an important part in boundary lubrication. Vegetable oils possess good oiliness, high viscosity index and low coefficient of static friction. On account of these valuable properties, various types of vegetable oils either alone or in admixture with mineral oils have been recommended for different lubricating purposes. Castor oil as such is considerably employed by various railways in India as a lubricant. Bhatnagar and Ward²⁶ solved the 'Hot Axle Problem' on Indian railways. They found that by avoiding the production of gummy and resinous materials during controlled oxidation of rape-seed

6
9/18/89

CHECKED

28.4.97

C. F. T. R. I. LIBRARY, MYSORE.

Acc. No. 2396

Call No. F8,4 "p2 N51

CHECKED
2008
✓

Please return this publication on or before the last DUE DATE stamped below to avoid incurring overdue charges.

VERIFIED
2013
✓

Due Date	Return Date	Due Date	Return Date	Due Date	Return Date
~~10.7.86~~		1.11.86	4.11.86		
2.7.86	9.7.86	16.12.86	16/12		
24.7.86	24.7.86	6/2/91	5.2.91		
8.8.86	V/V				
23/V	28/8/86				
12/9/86	15/9				
~~31.9.86~~					
1.10.86	3.10.86				
18.10.86	17.10.86				

CFTRI-MYSORE



2396

Proceedings of t

Acc. No. 2396

F8,4"p2 NSI

AT. CHEM. LAB

Symp. on

Fats &

m. 1951

